ADSORPTION EVALUATION OF CROSS-LINKED POLYMERS FOR WATER TREATMENT

BY

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To my family

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ABSTRACT

Full Name : Musa Auwal Muhammad

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N,N-diallyl-N-sulfopropylammoniopropylphosphonic acid and a cross-linker using tert-butyl hydroperoxide (TBHP) initiator to give cross-linked polyzwitterion (CPZ). The cross-linked polyzwitterion/dianion (CPZDA) was accessed by the treatment of CPZ with NaOH. New hydrophobic cross-linked dianionic Polyelectrolytes (**HCDAP**) was synthesised by cyclopolymerization involving N, N-diallyl-N- aminomethylphosphonic acid and a crosslinker using 2,2-Azo-*bis*-isobutyronitrile (AIBN) initiator to give hydrophobic cross-linked polyzwitterionic acid (**HCPZA**). Hydrophobic cross-linked dianionic Polyelectrolyte (**HCDAP**) was accessed by the treatment of **HCPZA** with NaOH. The adsorption efficiency of the resins were evaluated for Ni^{2+}, Co^{2+}, Cd^{2+}, and Cr^{3+} from water. Influence of temperature, contact time, pollutant concentrations, sorbent dose and pH were investigated for the optimum conditions as well as thermodynamic and adsorption kinetics. The experimental data fitted Langmuir, Freundlich and Temkin isotherms. The adsorption activity of the polymers was tested under optimum treatment conditions for real wastewater.

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N,N-diallyl-N-sulfopropylammoniopropylphosphonic acid and tetraallylpiperazinium dichloride (from allylchloride and piperazine) تم copolymerized المركبين معا باستخدام (TBHP), التي اعطت cross-linked polyzwitterion (**CPZ**). وعند تفاعلها مع NaOH ينتج **CPZDA**

تم تحضير (**HCDAP**) cross-linked dianionic Polyelectrolytes جديد غير محب للماء , باستخدام cyclopolymerization الذي يحتوي ويشارك بذرة N .

N-diallyl-N-sulfopropylammoniopropylphosphonic acid و استخدام – a cross linker

2,2-Azo-*bis*-isobutyronitrile (AIBN) مبادر (محرض) لكي يتم انتاج cross-linked polyzwitterionic acid (**HCPZA**). غير محب للماء .

cross-linked dianionic Polyelectrolyte (**HCDAP**) الغير محب للماء تم الوصول اليه من خلال معالجة **HCPZA** مع NaOH . الناتج النهائي تم استخدامه في إزالة Ni^{2+}, Co^{2+}, Cd^{2+}, and Cr^{3+} من الماء .

وقد تم التوصل الى الظروف المثلى لتأثير درجة الحرارة، ووقت الاتصال، وتركيزات الملوثات، جرعة المواد الماصة ودرجة الحموضة وبالإضافة الى الديناميكا الحرارية والامتزاز الحركي .

تم دارسه نشاط الامتزاز للبوليمر تحت الظروف المثلى للمياه العادمة .

CHAPTER 1

INTRODUCTION

1.1 Background

Introduction of foreign matters into the water bodies by various activities of both natural as well as human-induce processes has led to the deterioration of water making it unsuitable for desired purposes. One of such foreign matters are the heavy metals, which poses a serious health problems to humans as wells as other flora and faunas in the environment [1]. Viable water supplies are vital for various activities including agricultural, industrial, energy production, as well as domestic consumption. However, in a classic case of unintended consequences, contaminants such as organics, heavy metals are being added to environment and is now considered as a significant risks to groundwater and drinking water sources [2]. Recently, more stringent regulations for drinking water quality are being recommended to be implemented due to this developing trend [3]. Heavy Metal is any metal or metalloid of environmental concern and consider to be having toxic effect even at a very low concentration. The major elements in this category includes antimony (Sb), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Nickel (Ni) and lead (Pb) to mention few. They are found normally below the earth's crust in nature and are non-biodegradable. Heavy metals generally applied to wide range of pollutants usually encounter in soil and water [4]. Some of these metals are essential in low amount in humans and other animals and can only be toxic or poisonous when their concentration is higher than maximum allowable limits. Bioaccumulation of heavy metals in the biotic system is

the major health hazard attributed to them. Several industrial activities such as chemical manufacturing, electroplating, tannery, painting, mining, metallurgy, nuclear and other industries have contributed tremendously to heavy metals pollution [5]. Considering health impacts associated with heavy metals exposure identified by the United States EPA, more and more stringent regulations are been modified periodically to make sure that discharge from the above mention activities are well treated before finally release into the environment [6].

Contamination of environment by heavy metals can be trace back to ancient's civilization, where metals like copper, lead and mercury were used for various crafts by the Roman and Phoenicians. Nowadays, they are used extensively in areas such electronics, high-tech applications, machines, chemical manufacturing, electroplating, tannery, painting, metal-finishing, battery mining, metallurgy, nuclear and other industries as well as in artifacts of everyday life. With increasing generation of metals from above activities, the problem of waste disposal is of paramount importance. As a result, they are able to enter into the aquatic and food chains of humans and animals from a variety of human-induced activities as well as from the natural phenomenon such as weathering of soil and rocks. Cobalt is crucial in many industrial applications such as power plants, metallurgical processes, mining, tannery, pigments and paints etc. Cadmium has varieties of applications including in ceramics, photography, insecticides, electronics, metal-finishing industries and metallurgical industries and refined petroleum products [7-9]. Copper and Zinc are required as essential trace elements. Biological system uses copper in order for enzymes to function during plants photosynthesis while zinc is vital to human diet. High concentration of copper and zinc in the environment are usually associate with activities mentioned

earlier. Arsenic exist in two forms in the environment; oxidation state of +5 arsenate, and +3 arsenite. It occur natural as most of the elements and can be found both underground water and other water bodies as a result of natural and anthropogenic related activities. Chromium enters into the environment by natural inputs and anthropogenic sources. It exist in in form of Cr^{3+} and Cr^{6+} with the hexavalent chromium more toxic than trivalent chromium. Most of the heavy metals in aqueous environment occur as either cationic forms (Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Hg^{2+} , Pb^{2+}, Zn^{2+} etc.), oxoanions (AsO_4^{3-}, SeO_4^{2-} and CrO_4^{2-}) or in organic forms [$(CH_3)_2Hg$]. A number of metal ions namely arsenic, chromium and selenium, are found naturally in water bodies, but most of them originated from both domestic and industrial effluents[10]. Having of these metals in both water bodies and soils at elevated concentrations is not acceptable as they tend to persist and bioaccumulation problems in aquatic organism tissues, making imperative for their quantitative removal and as well a continuous monitoring (concentration) [9]. As such the World Health (WHO) has listed four of these as priority elements (As, Cd, Pb and Hg) of major 'public health concern' along with six other chemicals [14].

Therefore, it is expected that in the near future many water plants in the world will have to improve treatment technologies. There is a need for improvement in the efficiency of water purification techniques. Conventional methods available for removal heavy metals commonly found in drinking water and wastewater effluents include filtration, phytoremediation, electrocoagulation, ion exchange, electrochemical treatment, membrane technology [11, 12]. The treatment effectiveness of these methods might be hindered sometimes when the metals are at very low concentrations. Cost implication is another

factor to be consider on the choice among the several technologies are available as well as their efficiency, ease of operation among others.

1.2 Statement of the Problem

With the extensive industrialization and urbanization going on in the country, the quality of limited groundwater resources is being endangered by chemical pollution especially from heavy metals. The limited available water supplies are contaminated from various types of industrial waste and disposal practices. Large volume of water used by the industries for processing can potentially pollute waterways as a result of discharge of waste by the industries into streams, rivers, runoffs and seepages of stored waste into nearby water sources with high likely to be present in groundwater sources. Considering the health impacts associated with heavy metals exposure, there is a much greater need to protect the limited water resources from deteriorating in quality as a result of them. Since it is strongly recommended that pollutants should be eliminated if not completely removed from wastewater efficiently prior discharge, different remediation technologies are being applied for water treatment such electrocoagulation, membrane filtration, ion exchange etc. each have recorded varying levels of success and inherent limitations in removal of heavy metals.

1.3 Significance of the Study

In a country like Saudi Arabia that is faced with shortage of freshwater resources, it is imperative that water is kept free from pollution in order to partly ease the effects of water scarcity. With the extensive industrialization, urbanization and other activities drive being pursued in the country, the quality of limited groundwater resources as well as surface

water are threatened by pollution from various toxic pollutants. There is a need to develop techniques which are environmentally friendly, simple-to-use, effective and efficient in removing pollutants from water. Adsorption technique using polymeric sorbents are been considered to be effective method in removing pollutants from wastewaters. This creates the opportunity for further research in exploring the structural properties of various synthetic materials in removing toxic metals and other pollutants commonly found in water.

1.4 Research Objectives

This research was primarily aimed at evaluating the efficiency of synthesized cross-linked polymers as adsorbents for metal ions removal in water. Therefore, the following key objectives were drawn.

1. To demonstrate removal of Nickel (Ni), Cobalt (Co), Cadmium (Cd), and Chromium (Cr) from contaminated water using the synthesized Cross-linked polymers.

2. To determine optimum conditions (i.e. kinetic parameters) that include adsorbent loading, temperature, medium pH, contact time and concentration of heavy metals.

3. To monitor adsorption chemistry (i.e. kinetics) under the identified optimum conditions.

4. To test the removal capacity of heavy metals by the synthesized polymers from real wastewater under the optimum treatment conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

This is a term given to any metal or metalloid (semimetal) that has a density between 3.5 to 7 g/cm^3 and consider to be having toxic effect even at a very low concentration. The earlier mention elements in this category includes Cadmium (Cd), Cobalt (Co), Chromium (Cr), and Nickel (Ni) etc. They are found normally below the earth's crust in nature and non-biodegradable. The term generally applied to wide range of pollutants usually encounter in soil and water [4]. At a very low concentrations, these metals are essential in to humans and other animals and can only be toxic when they are above the allowable limit. Bioaccumulation of these metals in the biotic system is the major health hazard attributed to them is of concern [5].

2.2 Sources of Heavy Metals

Heavy metals differs widely in their physical and chemical properties as well as application. As such various areas such electronics, high-tech applications, machines, Chemical manufacturing, electroplating, tannery, painting, mining, metallurgy, nuclear and other industries as well as in artifacts of everyday life are the common source of heavy metals. Due to the variety of their uses, they are able to enter into the aquatic and food chains of humans and animals from a variety of anthropogenic as well as natural processes such as weathering of soil and rocks. The major contributors of heavy metals into the

environment includes mining, landfill, municipal wastewater, runoff and industrial effluents, specifically that of battery, electroplating and metal-finishing industries. Looking at the increase in metals generation stemming from technological activities, the problem of waste disposal has become one of paramount importance.

Metal ions levels in most cases is beyond water quality criteria put in place to protect humans, animals and environment. This is compounded by the tendency of metals being transported together with sediments, and their persistent nature (bioaccumulate and biomagnification in the food chain). Lead has been used in car batteries manufacturing, as a protective shield for radiation, paints, and other applications in the industries. it has also been used in plumbing as well as an additive to gasoline which decreased substantially mainly because leaded gasoline has been banned or Phase in most countries [13]. Cadmium is used in electroplating, solders, batteries, TV sets, ceramics, photography, insecticides, electronics, metal-finishing industries and metallurgical industries [7-9]. Nickel is found naturally in soils and volcanic rocks. Various compounds of Nickel are used for a number of industrial applications which includes electroplating, automobile and aircraft parts, batteries, coins, spark plugs, cosmetics and stainless steel, and production of nickel‑cadmium batteries on an industrial scale. Other routes of entering into the environment through weathering of rocks and soils and leaching of the minerals [8]. Arsenic exist in two forms in the environment, arsenate, As (V), and arsenite, As (III) and naturally occur as most of the mentioned elements and found in underground water and other water bodies. The Minamata disease is associated with the toxicity of mercury is well recognized. Extensive use of chromium compounds in industrial applications has discharged huge amounts of wastewater containing toxic chromium species into water bodies. Chromium

enters into the environment through natural inputs and as well as human-induced sources. Volcanic eruptions, geological weathering of rocks, soils and sediments are the natural sources of chromium, whereas anthropogenic contributions of chromium come from the burning of fossil fuels, production of chromates, plastic manufacturing, electroplating of metals and extensive use in the leather and tannery industries [14].

2.3 Environmental and Health Impact

There are many toxic heavy metals presence in the environment as mentioned earlier, but the following are of specific major toxic effects. These are lead, mercury, arsenic, cadmium and chromium are more relevant in the present-day, industrially driven economies, and can carry public health and ecological concerns when found in the environment. They are the called five priority 'key heavy metals'. WHO has listed four of these priority elements (As, Cd, Pb and Hg) as chemicals of major 'public health concern' along with six other chemicals or groups of chemicals, namely air pollution, asbestos, benzene, dioxins and dioxin-like substances, inadequate or excess fluoride and highly hazardous pesticides [14]. Activities ranging from domestic to industrial processes contribute immensely to release the most of the heavy metals in the environment posing serious health problem to humans as well as flora and fauna. The presence of these metals in water and soils at elevated concentrations are not acceptable due to their health concern. Several past disasters have been reported related to heavy metals in aquatic environment. The Minamata event, reported in the mid-1950s, was due to methyl mercury contamination by the Chisso Corporation into Minamata Bay, Japan. Mercury accumulation in fish gradually poisoned human beings. Post World War II, contamination of cadmium in the Jintsu River in Japan

resulted in 'Itai-Itai' disease [8]. Later, in 1998, a Spanish nature reserve was permanently damaged by toxic metal wastes (Cu, Zn, Cd and Pb) from a mineral-producing plant [3].

2.4 Fate of Heavy Metals in Water

In the aquatic setting, most of the heavy metals exist in cationic forms (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}, Hg^{2+} and Pb^{2+}), oxyanions (e.g., AsO_4^{3-}, SeO_4^{2-} and CrO_4^{2-}) or organic forms [e.g., $(CH3)_2Hg$]. While some of the heavy metals, including arsenic, chromium and selenium, can occur naturally in water bodies but the highest percentage are of human related anthropogenic sources, including domestic effluents, landfill leachates and runoffs [10]. In waters, dry and wet deposition can be a significant source of heavy metals that were initially emitted to the atmosphere from geological (e.g., wildfires and volcanoes) and anthropogenic sources (e.g., motor vehicles, manufacturing industries and coal-fired power plants). Upon entering into the aquatic environment, heavy metals go through a number of physical, chemical and biological reactions, such as oxidation, reduction, absorption and adsorption, biological uptake and assimilation, precipitation and complexation, due to the presence of acid-base, aquatic organisms (microorganisms, plants, fish, small invertebrates) and soil. Some of these reactions transfer heavy metals from the hydrosphere to other environmental compartments (e.g., biological assimilation, adsorption to soil particles), but these reactions and subsequent movements are often reversible. Biological uptake and assimilation often causes accumulation of heavy metals in an aquatic organism in the water body (i.e., bioaccumulation) due to their rapid uptake and persistence [1, 12-13].

2.5 Toxicological Properties of Heavy Metals and Health Impact

Table 2. 1 Basic properties of priority toxic heavy metals

Element	Atomic number	Standard Atomic weight	Specific gravity	Category	Major Toxic effect
Chromium (Cr)	24	52.00	7.19	Transition Metal	Carcinogenicity [Cr(VI) only]
Arsenic (As)	33	74.92	5.73	Metalloid	Metabolic interference, organ failure, carcinogenicity
Cadmium (Cd)	48	112.41	8.65	Transition Metal	Osteomalacia, nephrotoxicity
Lead (Pb)	80	207.2	11.34	Poor metal	Neurotoxicity
Mercury (Hg)	82	200.59	13.53	Transition metal	Neurotoxicity ($[CH_3Hg]^+$)

Source: [15].

Heavy metals can present unique toxicological profiles, and with a long biological half-life for many of these metals, toxicity may occur at what are traditionally considered as low environmental concentrations. Some of the important toxicological effects of five heavy metals are summarized below.

2.5.1 Chromium

Chromium is a transition element has many industrial applications such as in alloys (e.g., stainless steel) and chrome plating due to its excellent corrosion resistance and hardness.

It can exist in valences of +2 to +6, and mainly present as chromium (Cr^{3+}) or as chromium(Cr^{6+}) in the aquatic environment depending on the redox potential [3]. While chromium (III) is an essential element (nutrient) with no known toxicity, chromium (VI) compounds are known human carcinogens. Even though evidences on the carcinogenic behavior of chromium (VI), including calcium, lead, strontium and zinc chromates, via the inhalation route [3], the toxicological relevance of its carcinogenicity via the oral route (i.e., consumption of contaminated food and water) exist, it still remain inconclusive and controversial especially at low dosages [16, 17]. Because chromium (VI) is an oxidizing agent, it is easily reduced to the non-toxic form i.e. chromium (III) by sulfides and thiols (reducing agent) in human gastric juice and rat liver microsomal fraction. Recent studies suggested that a cytotoxic mode of action would be dominant in the low-dose region where exposure to chromium (VI) by humans occurred through drinking water instead of a mutagenic mode of action[16].

2.5.2 Cadmium

Cadmium can be found in the aquatic environment as Cd^{2+}. It is closely related to zinc (a Group 12 element) and they often occur together. The major uses of cadmium include electroplating, anticorrosion agents, batteries and pigments[18]. Cadmium can be found in mining operation runoffs and electronic manufacturing and recycling wastes [19]. Although the acute toxicity of cadmium is relatively low, it is known that cadmium has a half-life of approximately 10–30 years, depending on the organ and tissues [20]. It accumulates primarily in the kidney[18]. According to the IARC, cadmium is 'probably carcinogen' (Group 2A) via inhalation, although no evidence of carcinogenicity or

genotoxicity via an oral route (i.e., drinking water and food consumption) has been found [21]. Toxic levels of cadmium seem to cause brittle bones, and put those affected in extreme pain. It is thought that cadmium mediates damage to bones indirectly by its interactions with organs in the body, and it can eventually lead to death through organ shut down, especially renal failure.

2.5.3 Lead

Lead occur naturally within the earth's crust and has been employed in many industries for applications such as in car batteries manufacturing, as a protective shield for radiation, paints, alloys, solder and pigments etc. It has also been used in plumbing and as octane booster for gasoline [13]. Lead exist in two valence states, namely +2 and +4, with the more stable form as Lead (II) and more common in the aquatic environment [15]. Lead compounds may enter the aquatic environment via surface run-offs, dry and wet deposition from the atmosphere. Lead has been used in pipes and fittings, as well as in soldered connections in water distribution systems, and in plumbing in residences[15]. The problem with lead is that its adverse effects on children are quite profound as it can hinder development in a child's mental capacity. It has been shown that the levels of lead leaching from soldered connections in water pipes could reach 210–390 mg L^{-1}, which is harmful enough to children [22]. By inhibiting haem synthesis through the disruption of iron inclusion in the complex, lead can cause a state of anaemia [23] while the inorganic forms of lead can be carcinogenic [21].

2.5.4 Cobalt

Cobalt like any naturally element in the environment can be found in rocks and soils. It is an essential element for living beings because it is associated with the synthesis of vitamin B12. Cobalt has been utilized in alloys, permanent magnets, paint-driers and in industrial catalysts. Soil and sediment contaminated with industrial pollution may contain high levels of cobalt. Chronic exposure to cobalt may cause goitre in human beings [24].

2.5.5 Nickel

Nickel is found naturally in soils and volcanic rocks. Other routes of entering into the environment through weathering of rocks and soils and leaching of the minerals [8]. Nickel and its salts serve in several applications, such as in electroplating, automobile, aircraft parts, batteries, coins, spark plugs, cosmetics and stainless steel [25]. The major sources of nickel in the environment are metal refining and production of steel.

2.6 Remediation Technologies

Several technologies available in the market can remove a wide range of metals commonly found in drinking water and wastewater effluents. Most available remediation techniques are expensive due to its unique characteristics of heavy metals high solubility, mobility and resistance to biodegradation. Different remediation options are currently available and are summarized below.

2.6.1 Phytoremediation

Bioremediation (phytoremediation) for the removal heavy metals is a cost-effective technologies that have been successfully in the treatment of wastewater [26].

Phytoremediation involves the use biological systems (plants, animals and microorganisms), to clean-up of pollutants from the environment [27]. The process use hydroponically grown plants in removing heavy metals from water [28]. Aquatic macrophytes (Typha, Azolla and Lemna) were reported by [26] as a promising wetland plants for removal of heavy metals. Bioremediation is the technological process whereby biological systems, plants and animals, including microorganisms, are harnessed to effect the cleanup of pollutants from environmental matrices [27]. Microbe-assisted bioremediation and phytoremediation of heavy metals are cost-effective technologies and metal ion accumulating plants have been successfully used for the treatment of wastewater [26]. Many researchers have reported that aquatic macrophytes viz. Typha, Phragmites, Eichhornia, Azolla and Lemna are potential wetland plants for removal of heavy metal and metalloids due to their morphological change [26].

2.6.2 Electrocoagulation

Like other treatment techniques, the application of electrocoagulation for heavy metals removal is feasible on an industrial scale [29]. The technique could be employed for the purification of water containing varieties of impurities including dyes, pigments and metal ions and associated contaminants [30-33]. Electrocoagulation consists of electrodes that act as the anode and cathode, where oxidation and reduction takes place. Many physicochemical processes such as oxidation, reduction, coagulation and adsorption govern the electrocoagulation [34]. Similarly to other treatment techniques, the electrocoagulation of heavy metals offers a cost-effective and easy-handling technique on an industrial scale [29]. Therefore, its critical evaluation at both the laboratory and industrial scales could provide an opportunity for large scale applications in water

purifications [30, 31]. Recent works by Golder and co-workers can be viewed as good examples of the process efficiency for water purification [32, 33].

2.6.3 Ion Exchange

Ion-exchange provide an effective way for treatment of wastewater effluents [35]. Lee and coworkers used Diphonix resin for the removal of ferric iron from solution [36]. Lasanta et al. investigated the ionic exchange of Fe^{3+} in different solutions using a chelating ion exchange resin [37]. Lee and Nicol have employed Diphonix resin to removal iron (III) from solution [36]. Lasanta et al. studied the equilibrium diagrams for ionic exchange, which occurs between Fe^{3+} in different solutions by a chelating ion exchange resin [37]. Khalil and co-workers monitored the removal of Fe (III) species, employing cross-linked chitosan resins immobilized with diethylenetriamine and tetraethylenepentamine. It had been found that the tetraethylenepentamine containing chitosan resin showed a higher uptake capacity towards Fe (III) compared with diethylenetriamine containing chitosan resin. [38].

2.6.4 Heterogeneous Catalysts and Catalysis

The work of Honda and coworker in the seventies, pave way to the dawn of photocatalysis leading to its application in water treatment[39, 40]. In view of their discovery, a number of studies were conducted on TiO_2 photocatalyst [41, 42]. Typically, in a photocatalytic system, a reaction induced by light occur at the surface of the catalyst resulting in either the adsorbate molecules or the catalyst substrate depending on where it occur. This is refer to as catalyzed photoreaction or sensitized photoreaction. The use semiconductor heterogeneous photocatalyst for the removal of Cr (VI) for wastewater treatment was

reported by [43, 44]. Testa and coworkers reported the reduction of Cr (VI) over TiO_2 in the presence of oxalate [45]. Chang et al. developed photocatalyst of Ag‑AgCl@TiO_2 for the removal of Cr(VI) [46].

2.6.5 Membrane Filtration

In this technique, a structurally designed membrane with active elements in nano scale is used. In recent membranes such as reverse osmosis, a uniform thin polymer is supported on a porous structure. This create a partition of water and other dissolved form between the membrane and most of the solution, allowing the movement of the water and dissolved substance through the membrane depending on its properties in term of chemical and physical. From the filtration point of view, substance such as colloids, organics and microbes as well as polymers can exist in nanoscale range which makes the membrane filtration possible. Hani et.al reported the removal of Cu(II) and Cd(II) ions using a combination of reverse osmosis and Nano filtration with high efficiency [47]. Similarly, the use of aromatic polyamide (ES 20) in low-pressure reverse osmosis membrane (ULPROM) for the removal of Cu^{2+}, Ni^{2+} and (Cr^{6+}) from water [48].

2.6.6 Adsorption

Adsorption can be defined as a process whereby a substance in liquid or gaseous phase formed a thin film on a solid surface. Usually the substance is adsorbate while the solid is the adsorbent. Among the technologies use to removed effluents in aqueous media, adsorption seems to have a great potential for such application. Recently, numerous investigations were documented on the exploitation of new adsorption derivatives for water treatment, especially when contaminated with metals. Adsorption is one of the key toxins-

removing method receiving attention today with great potential [49, 50]. George et.al, reported the use of cross-linked chitosan grafted with amido-carboxylic functional group for the sorption of Cu(II) and Cr(VI) with adsorption capacity of 318 mg/g [51]. Omri et.al achieved the removal of Mn(II) ions using activated carbons derived from Spinachristi seeds [52]. Agricultural residues were employed for the economical and efficient removal of Fe and Mn ions [53]. Since the adsorption performance is mainly limited by material design and properties, strong efforts have been done in exploring the structural properties of various materials. Grafting of functional groups to various material in order to bind metals in solution has been reported by many authors. Electrocoagulation have been reported [54-57], to removed effluents in aqueous media, adsorption [58, 59] seems to have a great potential for such application. Almond green hull was investigated by [60] for cobalt removal in aqueous solution. Graciela et al. reported cross-linked chitosan as an effective adsorbent for the removal of Cr species in limited time [61]. Johnson [62], reported the use of Peanut hull and Peanut hull pellets, achieving more than 75% removal of copper was removed within the first 20 min; while 92% at first 50 minutes. Similarly, Mehmet and co-workers studied the removal of Cu^{2+}, Ni^{2+} and Cr^{3+} by sawdust [63]. [64], demonstrated that the use of activated Carbon, Silica and Silica-AC Composite for removal of Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}. AC has more affinity to Cobalt ions (90% removal). Silica/AC (2:3) composite showed the greatest removal percentage for 30 & 200 ppm cobalt. Guo and coworkers use phosphate carbamate for the sorption of Cu^{2+} [65]. Polymers have been used extensively in wastewater treatment facilities, as such various authors put considerable efforts in order to develop a novel polymer adsorbent to increase the sorption performance [66-70]. Shaikh et al., uses cross-linked polyaminocarboxylates CAPE 6 and

CAPE 9 for the removal of Cu^{2+}, the resins showed excellent ability to adsorb the metal ions with efficiency removal at initial conc. of 200 ppb 77.5 and 99.4%, respectively [71]. Haladu et al., reported the use of cross-linked polymer CPZA 5 for Sr^{2+}. Junsheng *et al*. [72], investigated the activity of zwitterionic hybrid polymers on Cu^{2+} and Pb^{2+}respectively. Novel cross-linked polyzwitterionic phosphonate has been demonstrated by authors like [73]. [74], utilized cross-linked starch graft copolymer with aminoethyl group, in the removal of $cu^{2+}$and Pb^{2+} (II) ions was 75.5%, found at 21.05 and 144.08 mg/g, respectively.

The use of inorganic in combination with polymer hybrid materials for adsorption has been considered as promising, as it is effective, economical as well as environmentally friendly in removing pollutants from water looking at the number of studies conducted with new class of novel adsorption materials [68, 75]. Only, few studies reported the use the removal of both heavy metal and organic pollutants simultaneously [69, 76-78]. Co-adsorption method is vital in monitoring the process kinetics and evaluating the optimum factors. Therefore, it is required to have novel materials that combine two properties; hydrophobic domains and negative sites on its surface. Polyzwitterions, especially of N-derivatives, were employed form Sr ions removal [79]. Zwitterionic hybrid polymer reported by [80, 81] due to some excellent properties in term of structural flexibility, mechanical and thermal stability. These class polymers are of great scientific and technological interest; so far poly (diallyldimethylammonium chloride) alone document more than 900 patents and publications. Furthermore, an estimated of about forty (40) million pounds of the polymer are been sold and used annually for both water treatment palnts and other applications. The interesting thing about this, is electrostatic attraction that occur between the positive

quaternary ammonium polyelectrolytes and negative macro-ions, surfactants, leadin to different materials design in membranes, modified surfaces, and coating particles [82]. Shaikh et al., uses cross-linked polyaminocarboxylates CAPE 6 and CAPE 9 for the removal of Cu^{2+}, the resins showed excellent ability to adsorb the metal ions with efficiency removal at initial conc. of 200 ppb 77.5 and 99.4%, respectively [71].

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals and Materials

Nickel (II) (1000mg/L), Cadmium (II) (1000mg/L), Cobalt (II) (1000 mg/L), Chromium (III) (1000 mg/L), HNO_3, HCL, NaOH were from BDH Laboratory. The standard stock solutions were diluted to various concentrations as required for the experiment. An organic 2,2-Azo-*bis*-isobutyronitrile (AIBN) (with 70 w/w % in water), Tertiary butyl hydroperoxide (TBHP) (with 70 w/w % in water), diallylamine (≥ 98 % purity), Dimethylsulfoxide (DMSO), piperazine (97 % purity), allyl chloride (98% purity), 1, 3-propanesultone (≥98% purity) from Fluka (AG) and used as received. Monomers **1** [83] and **2** [84] were synthesized using literature procedures [83, 84]. Briefly, monomer **1** was synthesized by the reaction of propanesultone and diethyl 3-(diallylamino)propylphosphonate followed by ester hydrolysis [83]. Monomer **2** was obtained by reacting allyl chloride with piperazine [84]. Hydrophobic monomers **2** [85] and cross-linker **3** [86] were synthesized using literature procedures [85, 86]. Monomer **1** was prepared in our laboratory using by reacting dimethyl glutamate with allyl chloride followed by hydrolysis of the ester groups. All reagents were purchase from commercial vendors and are of analytical grade used without purification as received. Laboratory wares used in this experiment are in-house and are of required standard. Distilled water was utilized throughout.

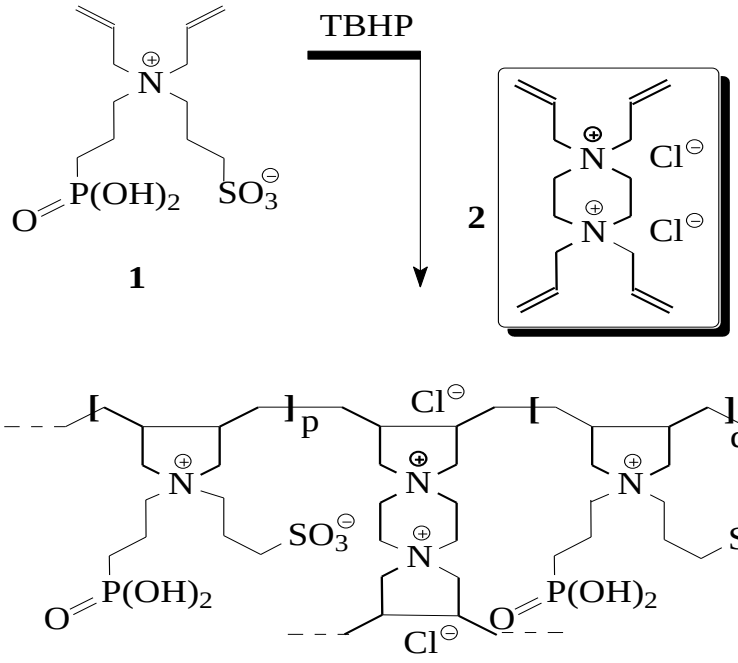
3.2. Synthesis of the Polymers

3.2.1 Copolymerization of 1 and 2

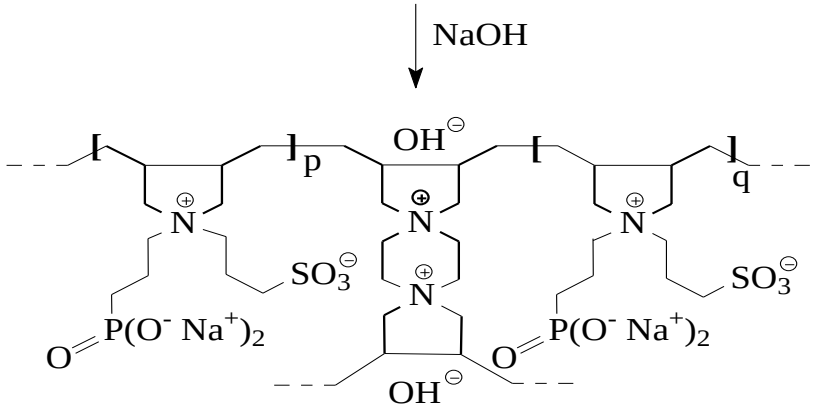
The monomer **1** (10.53 g, 30.85 mmol) and cross-linker **2** (1.1 g, 3.45 mmol) were dissolved in deionized water followed by the addition of TBHP (640 mg). The mixture in a closed flask was stirred for 22 hours at 95 °C. After several hours the magnetic stir-bar became static. The swollen soft solid was transferred to water and allowed to soak with repeated change of water. The resin **3** was soaked in acetone, filtered and dried *in vacuo* at 70 ^{o}C (5.1 g, 49%).

3.2.2 Transformation of CPZ 3 to cross-linked polyzwitterion/dianion CPZDA

CPZ **3** (5.48 g, 16.2 mmol) mixed with sodium hydroxide (1.94 g, 48.6 mmol) in water (50 ml) were stirred for 2 h. After adding excess methanol, resin **4** was filtered and then dried *in vacuo* at 65 ^{o}C and obtained as a grey colored powder (5.2 g, 85 %).



3: Cross-linked polyzwitterion (CPZ)



4: Cross-linked polyzwitterion/dianion (CPZDA)

Figure 3. 1 Synthesis of cross-linked polyzwitterion/dianionic polymers

3.2.3 Diallylaminomethylphosphonic acid 2

Monomer **1** was synthesized as described in the literature with additions of some new parts in procedure [87]. Thus, diallylamine (**1**) (0.35 mol) was gently added drop wise manner for 45 minutes to a mixture of phosphorous acid, water and concentrated HCL in order of (0.35 mol), (35 mL) and (35 mL) in ice. Refluxing of the mixture for 1 hour and solid paraformaldehyde (0.70 mol) and water (35 mL) were added independently in various portions (ca. 20 minutes). The solution obtained from the above reactions was then refluxed for 1hour and finally freeze-dried to get the crude product **2** along with excess formaldehyde. The crude product was taken up in water (100 mL); the precipitated formaldehyde powder was filtered out and the filtrate was evaporated at 80°C. The residual thick liquid undergoes further drying under vacuum to fixed weight to in produce **1** as a light yellow viscous liquid (72 g, 90%). A hydrogen-1 NMR spectra of a fixed mass of crude product and ethanol of known weight in Deuterium oxide (D_2O) confirm how pure purity the product is. Signals of CH_2P- of **2** at δ 3.11 versus CH_2O of ethanol at δ 3.40 give us purity and molar mass of the product obtained was 230.3 g mol^{-1} as against the computed value of 227.63 g mol^{-1} confirms the structure of 2 as the HCl salt. Monomer **2** was thus pure enough to be used directly for the subsequent polymerization reaction without the need further purification.

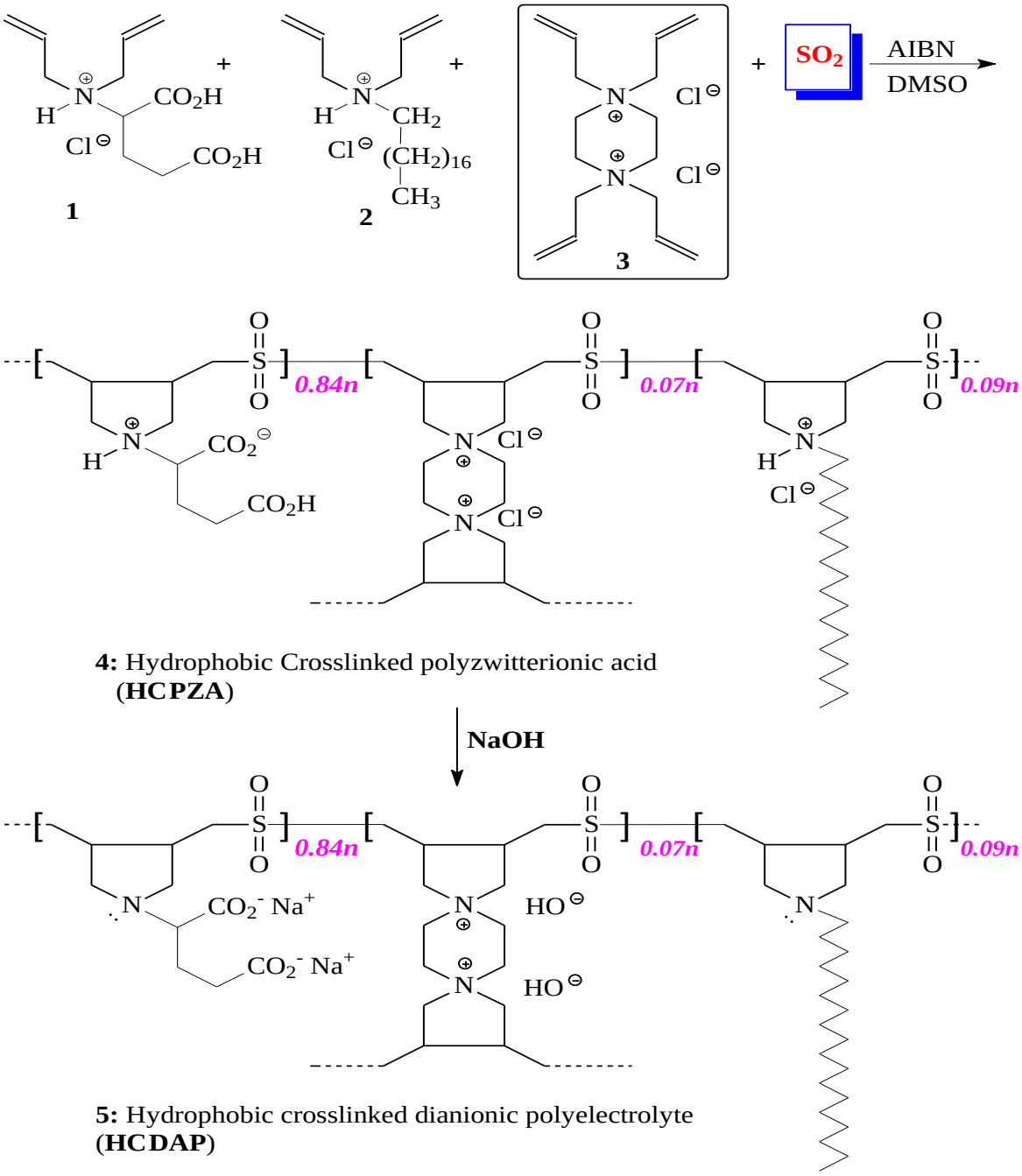
3.2.4 Tetrapolymerization of monomers 2, 3, 4 and SO_2 to HCPZA 4:

To a solution of **2** (9.83 g, 43.2 mmol), **3** (1.82 g, 4.71 mmol), and **4** (1.13 g, 3.54 mmol) in dimethyl sulfoxide (21 gram) in a R B flask (50 cm^3) was absorbed SO_2 (3.52 g, 55 mmol). Initiator AIBN (326 mg) was then added to above mixture and stirred a closed flask at 65ºC for 48 hour. The transparent gel was soaked in water; the white resin was

repeatedly washed with water and then finally with acetone. The final product has a fixed weight (13.2 g, 81%) after vacuum drying at 60ºC for 6 h. The resin has the following composition: C, 36.2; H, 6.4; N, 5.2; S, 11.3. The incorporated monomers as in HCPZA **5** containing **2** (84.0 mol%), **3** (9.15 mol%), **4** (6.88 mol%) and SO_2 (100 mol%) requires C, 36.94; H, 6.13; N, 5.40; S, 11.78%. $\nu_{max.}$ (KBr) 3420, 2925, 2853, 2360, 1705, 1646, 1467, 1410, 1308, 1128, 1074, 915, 756 and 535 cm^{-1}.

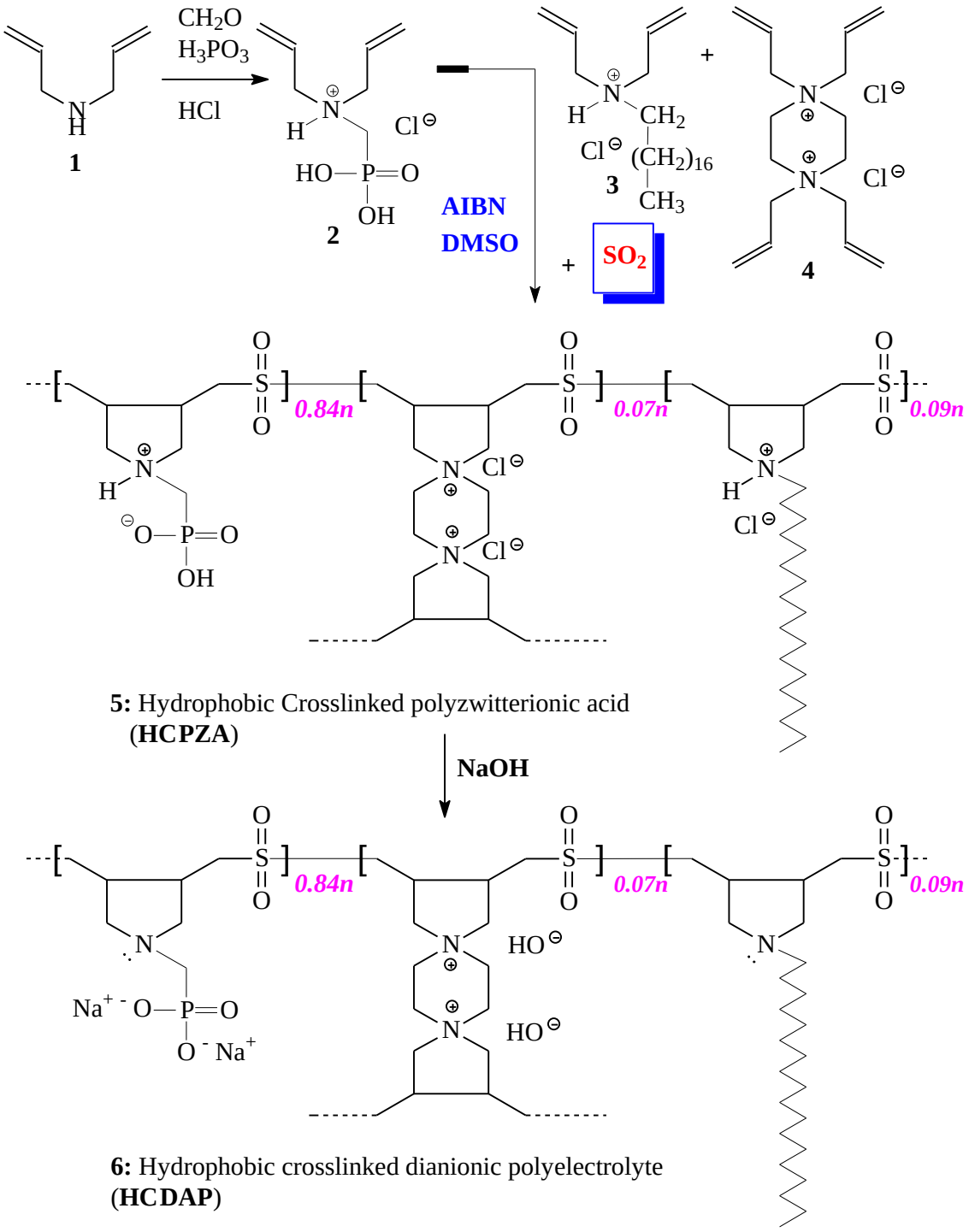
3.2.5 Tetrapolymerization of monomers 1-3 and SO_2 to HCPZA 4:

To a solution of **1** (8.45 g, 32 mmol), **2** (1.37 g, 3.56 mmol), and **3** (0.855 g, 2.68 mmol) in dimethyl sulfoxide (14.5 g) in a round bottom flask (50 cm^3) was absorbed SO_2 (2.62 g, 41 mmol). Initiator AIBN (250 mg) was added and the mixture was stirred in the closed flask at 65ºC for 48 hours. A few times the flask was opened to release gaseous product N_2. The transparent gel was soaked in water and was repeatedly washed with water and finally with acetone. The resin was subjected to vacuum drying at 60ºC for 6 hours with a constant weight (11.3 g, 85%). Composition of the resin was found to be: C, 46.3; H, 6.8; N, 4.7; S, 9.9. The incorporated monomers as in HCPZA **4** containing **1** (84 mol%), **2** (10 mol%), **3** (7 mol%) and SO_2 (100 mol%) requires C, 47.37; H, 6.42; N, 4.83; S, 10.47%. $\nu_{max.}$ (KBr) 3440, 2925, 2853, 2671, 1724, 1622, 1453, 1404, 1306, 1126, 1019, 951, 859, 765, 628 and 507 cm^{-1}.



Scheme 1. Synthesis of a hydrophobic cross-linked polyzwitterion/anion resins.

Figure 3. 2 Synthesis of Hydrophobic cross-linked polyzwitterion/anion polymer



Scheme 1. Synthesis of a hydrophobic cross-linked polyzwitterion/anion resins.

Figure 3. 3 Synthesis of Hydrophobic cross-linked polyzwitterion/anion polymer

3.3 Characterization of the Polymers

In order to ascertain the polymer structure and properties, both microscopy and spectroscopic techniques were utilized in characterizing the prepared materials in terms of surface morphology, elemental content thermal stability and stability in solution using tools of SEM-EDX, TGA, ZPA and FT-IR spectroscopy. ^{1}H- and ^{13}C-NMR spectra were measured respectively. The characterization tools were used to characterize the surface morphology of the polymer and elemental spectrum to get elemental analysis of the pristine polymer and metals-loaded polymers. Thermo Scientific iCE 3000 atomic absorption spectrometer (AAS) was utilized to monitor the concentration of the various metal ion using appropriate lamps. ICP-MS technique was employed to analyze the real wastewater samples. Infrared spectra were recorded on a spectrometer Thermo Scientific Nicolet 6700. Thermogravimetric analysis (TGA) for the resin was employed using a thermal analyzer SDT-Q600, TA instruments, USA elevating the temperature at a fixed rate of 10°C/min over the range of 30–700°C flowing at a rate of 100 $mLmin^{-1}$.

3.3.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

Brunauer−Emmett−Teller (BET) in cooled N_2 method by BET surface area analyzer was employed for the specific surface area measurements. Weighed Samples was degassed under vacuum for 6 hour at temperature of 80 °C. The process utilized the phenomenon of adsorption of Nitrogen gas on the polymer surface and the subsequent computation of the amount absorbed. The process of the degassing is aim at making sure the adsorbent surface is void of anything that might interfere with the surface area measurement. Specific surface area was calculated by the Brunauer−Emmett−Teller (BET) method, and pore volumes

were determined at the P/P0 =0.974 single point. Pore size diameter was determined by the BJH method.

3.3.2 Thermo-Gravimetric Analysis

Thermo-gravimetric analysis (TGA) was carried out using a thermal analyzer SDT (Q600, V20.9 Build 20 manufactured by TA instruments, USA). The polymer weighing ≈ 6 mg was taken in an aluminium crucible. The temperature was raised continuously at a uniform rate of 15 ^{o}C per minute and temperature range of 20–800 ^{o}C in a nitrogen atmosphere at 50 cm^3 per minute flow rate for the duration of the whole analyses.

Figure 3. 4 Thermo-gravimetric Analyzer

3.3.3 Scanning Electron Microscopy/Energy-dispersive X-ray spectroscopy

Scanning electron microscope (SEM) was used to characterize the surface morphology of the polymer before and after the adsorption of the heavy metals (Cadmium (Cd), Cobalt (Co) Chromium (Cr) and Nickel (Ni). Energy-dispersive X-ray spectroscope (EDX) equipped with a detector model X-Max was employed to obtain the elemental spectrum and to get elemental analysis of the polymers as well as; Cadmium (Cd), Cobalt (Co) Chromium (Cr) and Nickel-loaded polymers.

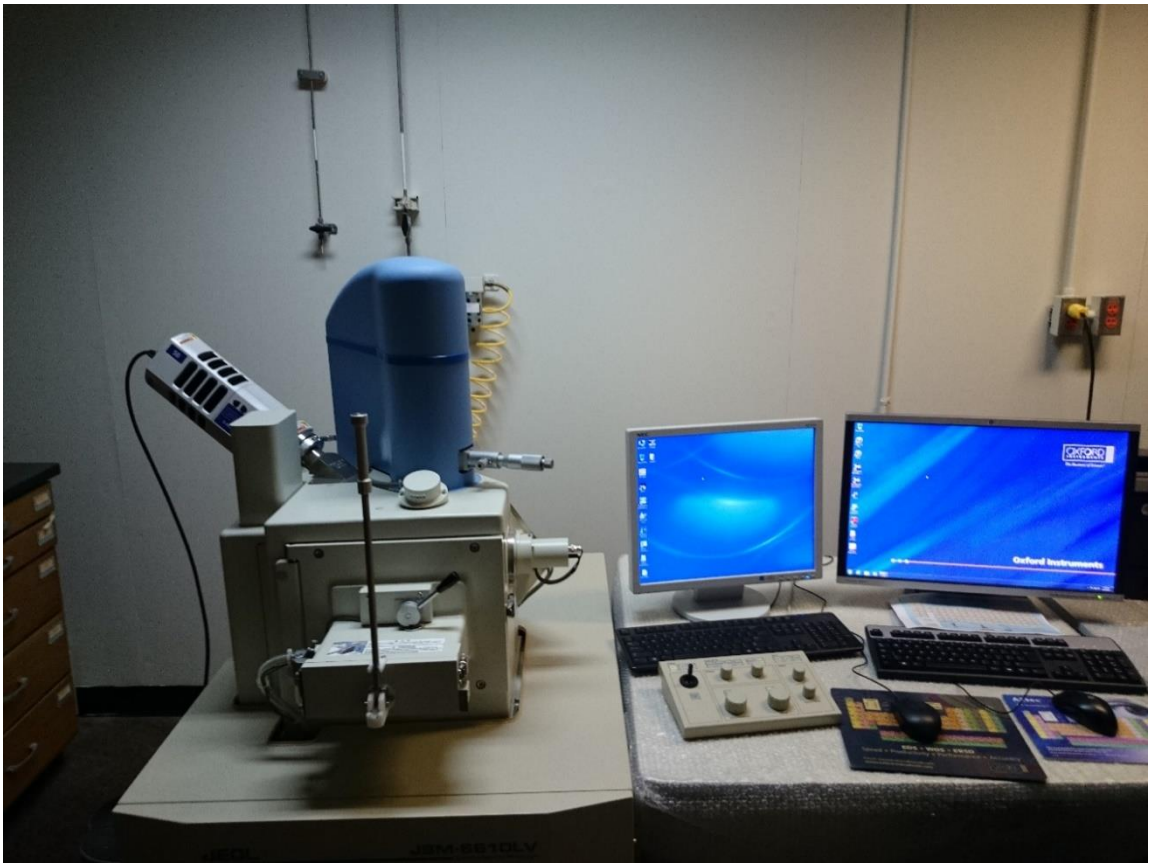


Figure 3. 5 Scanning Electron Microscopy/Energy-dispersive X-ray spectroscopy

3.3.4 Fourier Transform Infra-Red Spectroscopy

Fourier Infrared spectrometer (Thermo Scientific Nicolet 6700) was used to record the IR spectra from region of 400-4000 cm^{-1}. FT-IR spectroscopy was used as each material has a particular fingerprint based on the functional group within the material to identify it as well in the study to heavy metals adsorbed resin before and after the treatment.

Figure 3. 6 Fourier Infrared spectrometer

3.3.5 Zeta potential Analysis

Zeta potentials are often used as an important parameter in analyzing the electrostatic surface interaction in adsorption. A Zeta-Sizer Nano series ZEN2600 instrument (Malvern, UK) was used to measure the zeta potentials of the samples. To measure the zeta potentials of the cross-linked polymers, 10mg of each of the vacuum dried polymer was crushed to a fine powder and added to 100ml deionized water. The solution was placed inside a sonicator and was sonicated for 60 minutes. Sample of the solution was taken and the zeta

potential was measured. There were no addition of any background electrolyte to the sample before the analysis.

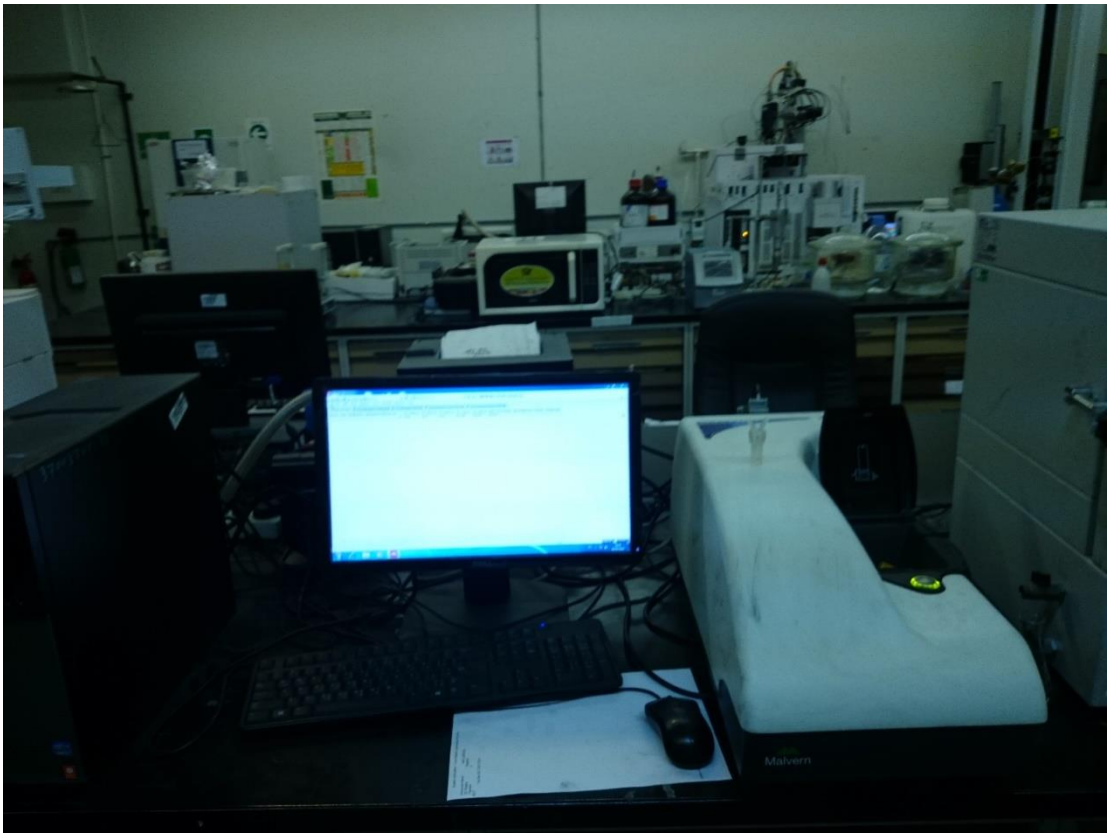


Figure 3. 7 Zeta-Sizer Nano series ZEN2600 Instrument

3.4 Instrumental Analysis

The resultant solutions from the batch adsorption were filtered and measured by Thermo Scientific iCE 3000 flame atomic absorption spectrometer (FAAS) equipped with a 10 cm air-acetylene burner. Inductively coupled plasma mass spectrometry (ICP-MS) model ICP-MS XSERIES-II Thermo Scientific, was used for the determination the metals concentrations of some metal in real wastewater samples.

Figure 3. 8 Thermo Scientific iCE 3000 flame atomic absorption spectrometer

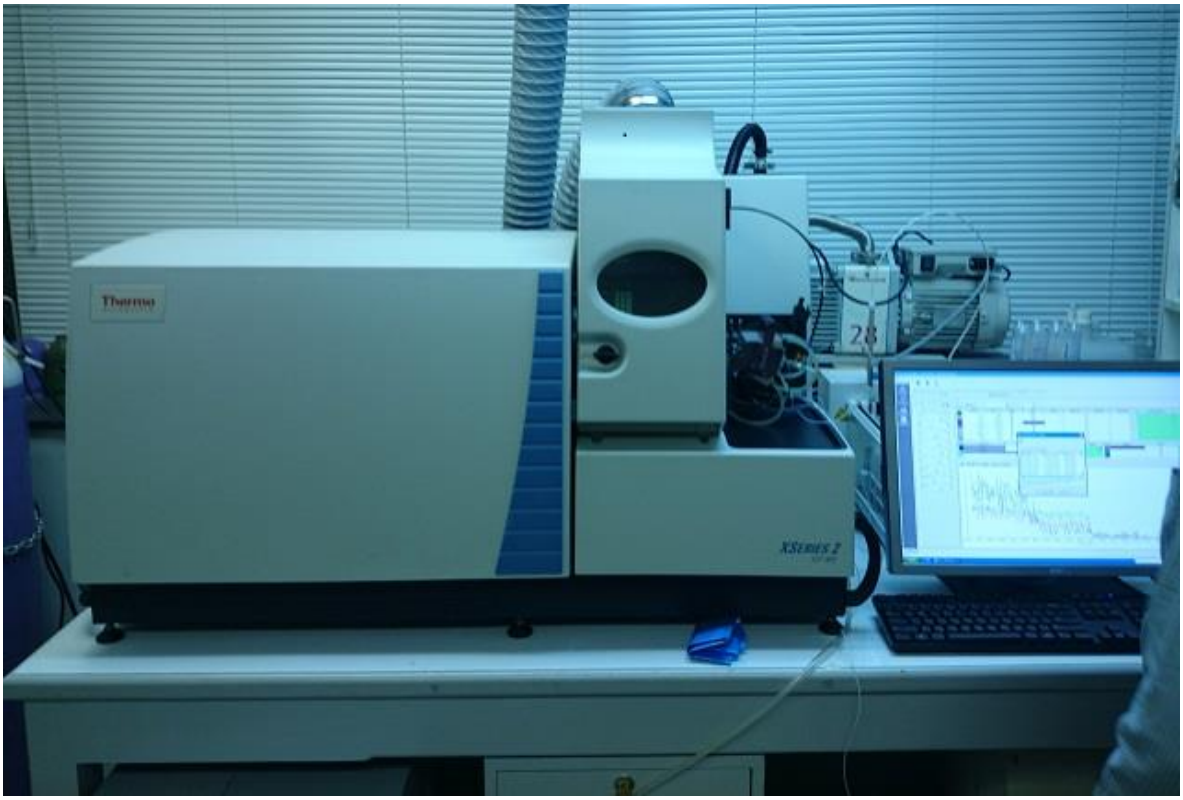


Figure 3. 9 inductively coupled plasma mass spectrometry (ICP-MS)

3.5 Preparation of Standard Solution

The standard stock solutions of Cobalt (II) (1000 mg/L), Nickel (II) (1000 mg/L), Chromium (III) (1000 mg/L) and Cadmium were diluted to various concentrations as required for the experiment. Laboratory wares used in this experiment are in-house and are of required standard. Distilled water was utilized throughout.

3.6 Batch Experiments

The adsorption behavior of the synthesized polymer was examined using an aqueous media containing ionic metal species. A predetermined adsorbent amount was added into 20 mL of Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^{2+} solutions into a container made of plastic and placed on a magnetic stirrer at 150 rpm until equilibrium was reached. Temperature effect on the adsorption behavior was also investigated by adjusting the bath temperature and thus, the solutions. The experiments are carried out as follow. A 30mg of adsorbent **HCDAP** or **CPZDA** were added in 20 mL of aqueous Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^{2+} , then stirred for period of 10,15, 20, 30, 40, 50, 60, 90 and 120 minutes respectively at 298K with concentrations ranging from 5 to 100 mgL^{-1}. Adsorbent dose of 10-50mg were used while the pH of the solution was adjusted appropriately during the adsorption (3-7). The resultant solution was filtered using a Whatman filter paper and the filtrate was analyzed by atomic absorption spectroscopy to determine the amount of metal ions uptake. Kinetic and thermodynamic behaviors were studied at 298, 313 and 333K respectively. Temperature effect on the adsorption behavior was also investigated by adjusting the bath temperature.

3.7 Data Analysis

The percentage (%) of removed Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+} ions after the equilibrium was computed by the equation:

$$\% \, Removal = \frac{C_\circ - C_e}{C_\circ} \times 100 \qquad (1)$$

q_e, (mg/g) is amount of metal ion adsorbed per unit mass of the resin at equilibrium and at time *t* (q_t, mg g^{-1}). Adsorption capacity was computed from as per the equations:

$$q_e = (C_o - C_e) \times \frac{V}{m} \qquad (2)$$

$$q_t = (C_o - C_t) \times \frac{V}{m} \qquad (3)$$

Given that C_0 (mgL^{-1}) denote the initial concentration, C_e and C_t (mgL^{-1}) are the concentrations at the equilibrium liquid phase and at any time *t*, V (L) stands for the volume, and m (g) is the resin mass. Given that:

- C_0 (mg/L) denote the initial Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^{2+} ions concentration;
- C_e and C_t (mg/L) are the Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^{2+} ions concentrations at the equilibrium liquid phase;
- V (L) stands as volume used of the solution and
- m (g) is the resin weight.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 Synthesis of the Polymers and Properties

The preparation process adopted utilized the principles of Butler's method in cyclopolymerizing monomer **1** (90%) and a cross-linker **2** (90%) to afford the cross-linked Polyzwitterion **CPZ 3** in good yield [88]. The polyzwitterion/dianionic resin **CPZDA 4** was finally obtained by the treatment of CPZ **3** with NaOH. The new resin features Zwitterionic as well as dianionic moieties on same repeating unit. Hence, the availability of the abundant anionic functionalities qualifies the resin to have metal adsorption capabilities. For **HCDAP**, hydrophilic monomers **1**, hydrophobic monomers **2**, and cross-linker **3**, also using SO_2 as the fourth monomer. This represents the first example of the incorporation of the hydrophobic monomer into cross-linked polymer cross-linked Cyclopolymers containing glutamic acid residues that can scavenge toxic metal ions with the assistance from its trivalent nitrogen and the hydrophobic surface of long chain (C_{18}) hydrocarbons to scoop up the organic contaminants. The resin has the following composition: C, 36.2; H, 6.4; N, 5.2; S, 11.3. The incorporated monomers as in HCPZA **5** containing **2** (84.0 mol%), **3** (9.15 mol%), **4** (6.88 mol%) and SO_2 (100 mol%) requires C, 36.94; H, 6.13; N, 5.40; S, 11.78%. $V_{max.}$ (KBr) 3420, 2925, 2853, 2360, 1705, 1646, 1467, 1410, 1308, 1128, 1074, 915, 756 and 535 cm^{-1}. The incorporated monomers as in HCPZA **4** containing **1** (84 mol%), **2** (10 mol%), **3** (7 mol%) and SO_2 (100 mol%) requires C, 47.37; H, 6.42; N, 4.83; S, 10.47%. $\nu_{max.}$ (KBr) 3440, 2925, 2853, 2671, 1724, 1622, 1453, 1404, 1306, 1126, 1019, 951, 859, 765, 628 and 507 cm^{-1}.

4.2 Characterization

4.2.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

For the BET surface area measurements, a fixed amount of sample was loaded into a BET glass sample holder, with the sample covered with a glass wool plug to prevent lost during analysis Brunauer−Emmett−Teller (BET) in cooled N_2 method using a Micrometrics ASAP 2020 BET surface area analyzer was employed for the specific surface area measurements. Samples were degassed under high vacuum for 6 h at 80 °C. Specific surface area was calculated by the Brunauer−Emmett−Teller (BET) method, and pore volumes were determined at the P/P0 =0.974 single point. Pore size diameter was determined by the BJH method. Table 4.1 gives the BET surface area and pore volume of the cross-linked polymers.

Table 4. 1 Brunauer-Emmett-Teller (BET) Surface Area Analysis of cross-linked Polymers

Polymer	**BET, m^2/g**	**Pore Volume cm^3/g**
CPZDA	25.4240	0.053988
HCPZA	0.0369	0.000163
HCDAP	26.3450	0.051

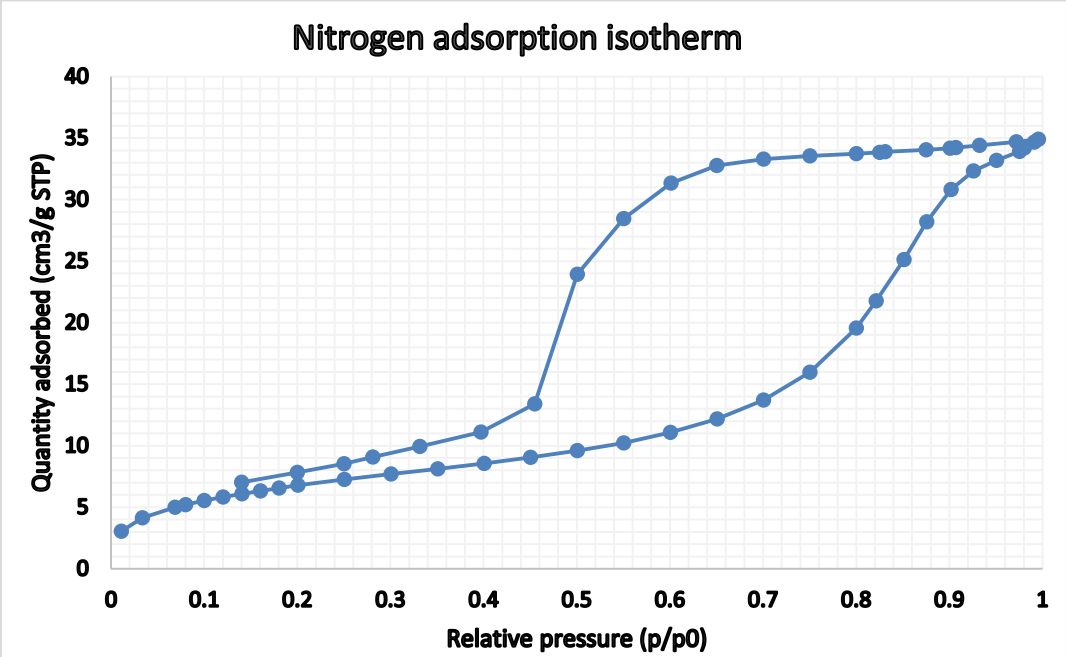


Figure 4. 1 Nitrogen adsorption isotherm.

4.2.2 Thermo-Gravimetric Analysis (TGA)

The first (16.6%) and the second (47.7%) major weight losses shown by the Thermogravimetric analysis (TGA) curve of **CPZDA 4** (Fig. 4.2) were due sulphur oxide elimination and carboxylate groups (pendant) degradation emitting species of CO_2, NOx and H_2O gases resulting from combustion of nitrogenated organic fractions respectively. At 800 °C residual mass was 35.7%, and is attributed to $Na_2O.1.5P_2O_5$ [70].

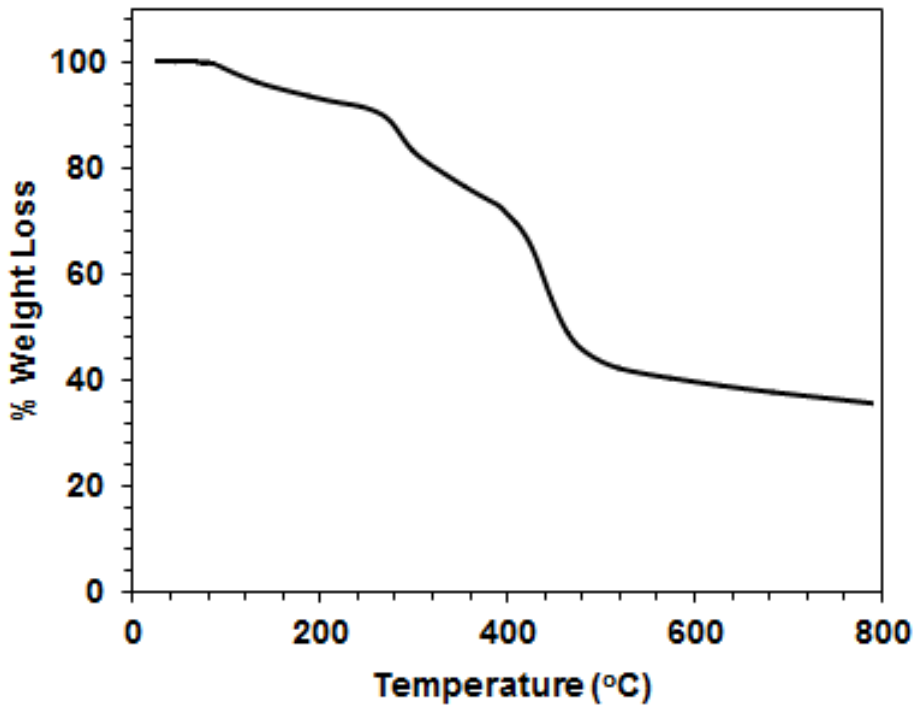


Figure 4. 2 TGA curve of CPZDA 4

TGA for curve of **CPZDA** (Fig. 4.2) were as a result to loss of SO_2 and decarboxylation of the pendant carboxylate groups with the release of CO_2, NOx and H_2O gases resulting from the decomposition of nitrogenated organic fractions respectively. Likewise the removal of moisture and water molecules embedded within the polymer. The remnant mass at 800 °C was established to be 34.7%, and belong to $Na_2O.1.5P_2O_5$ [70].

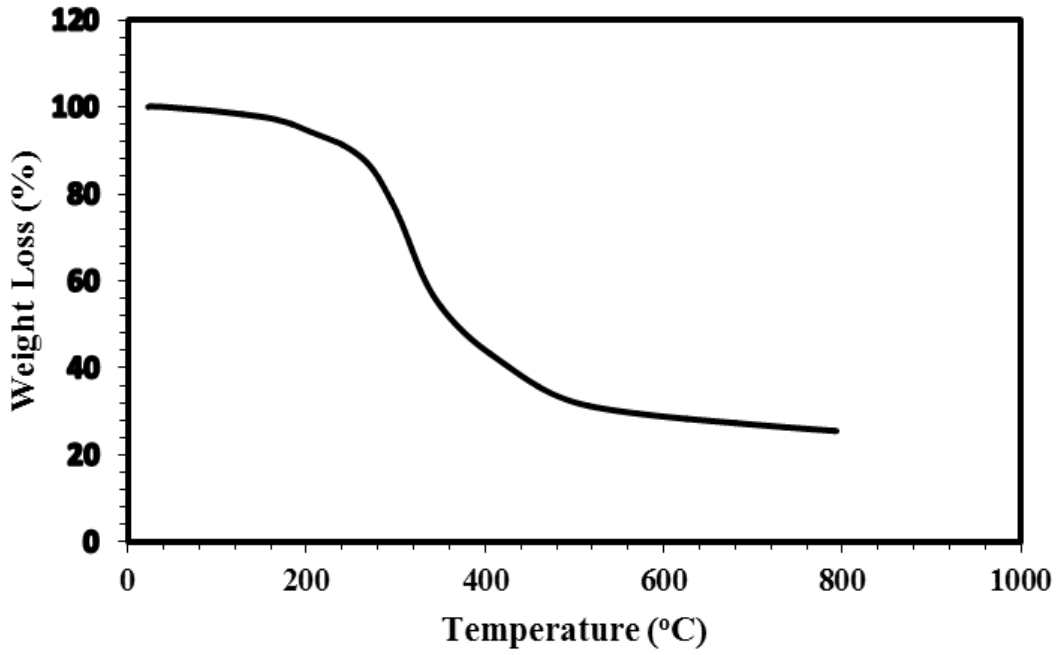


Figure 4. 3 TGA curve of HCDAP

TGA curve of **HCPZA** has three distinct weight loss steps. First was the slow but gradual weight loss of about 20% is attributed to the removal of moisture and water molecules embedded inside the cross-linked polymer. The second dramatic loss of about 25% around 320°C is attributed to the loss of SO_2 due to polymer degradation. The third slow and gradual loss of 15% is attributed to the combustion of nitrogenous organics with the liberation of NOx, CO_2 and H_2O gases [89]. At 800°C, the residual mass was found to be 28%.

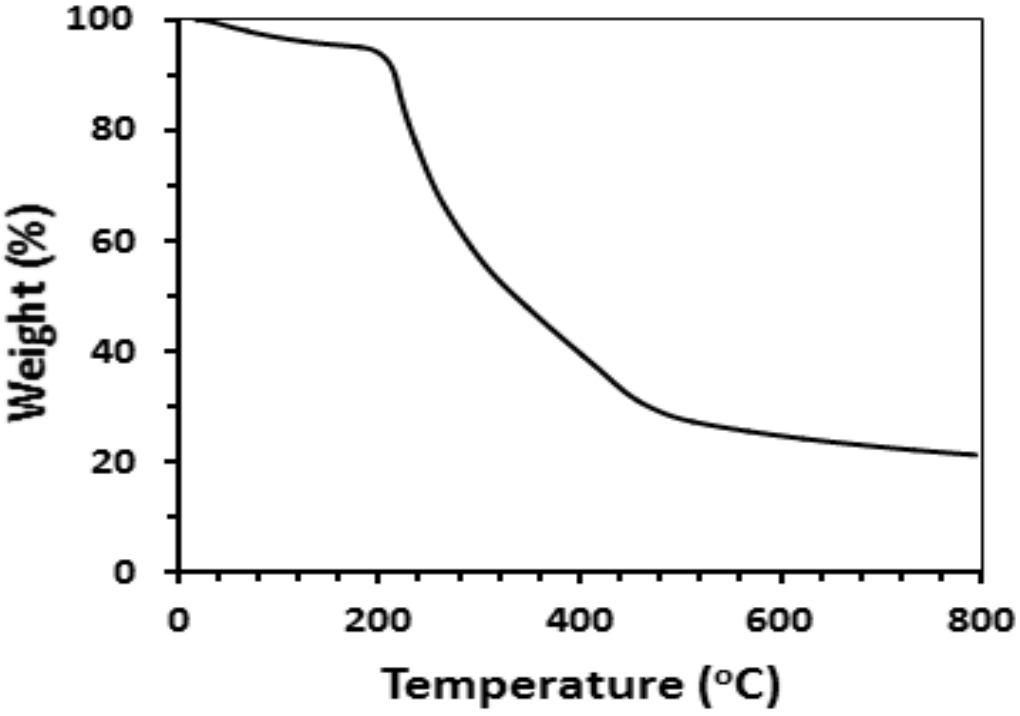


Figure 4. 4 TGA curve of HCPZA

4.2.3 FT-IR Characterization of Polymer

The IR spectrum of CPZDA **4** (Fig. 4.5a), absorptions around ~1216 and ~1040 cm^{-1} show the presence of sulfonate as well as phosphonate groups within the polymers [83]. The ~1466 cm^{-1} band could be attributed to C-N absorption. The peak at 1651 cm^{-1} was attributed to O-H vibration frequency in water molecule. Looking at IR spectrum of the resin after loading with nickel (Fig. 4.5b) displayed widening of absorption peak together with broadening phosphonate P-O stretching due to adsorption of the metal [90].

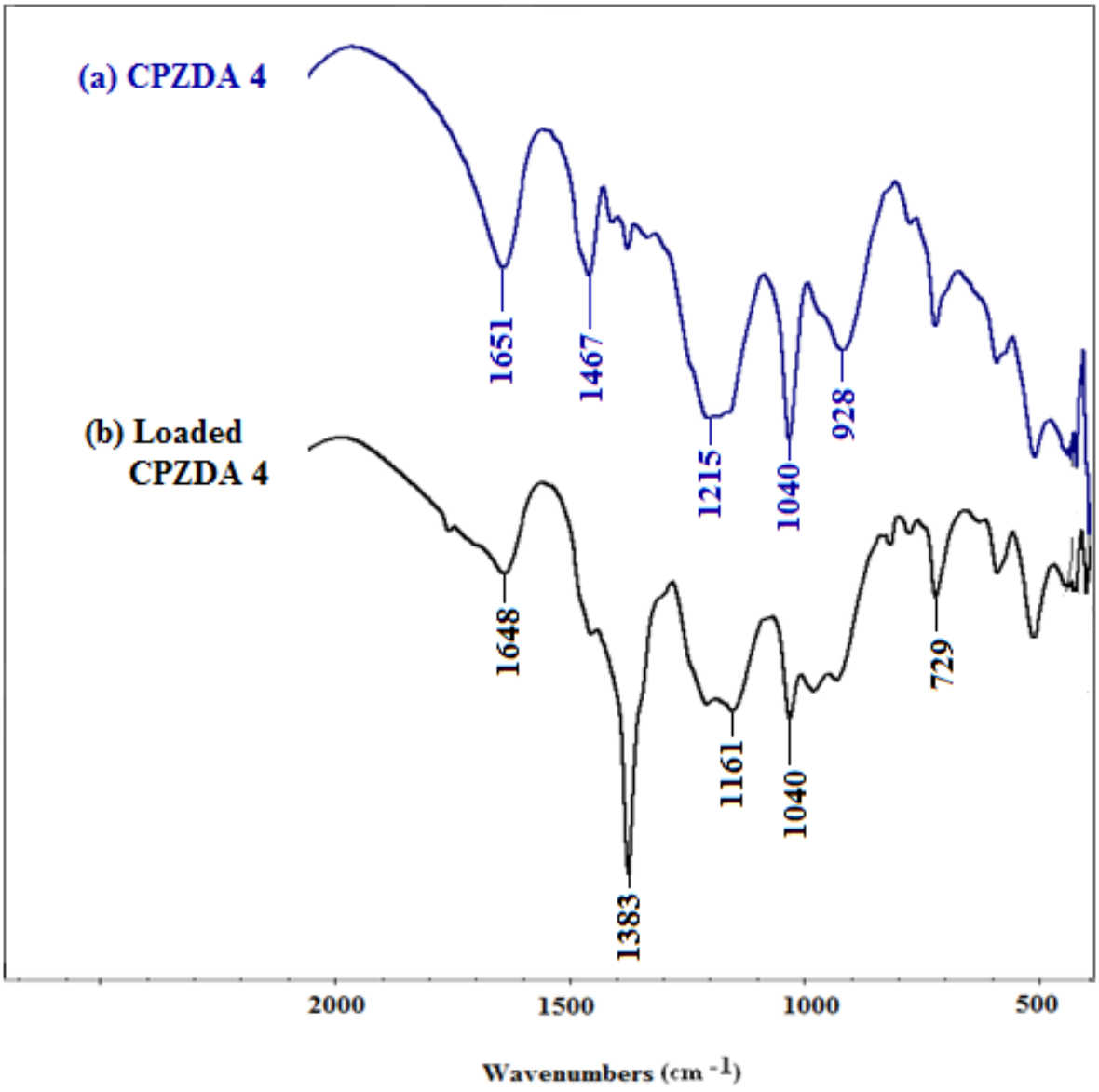


Figure 4. 5 IR spectra of (a) CPZDA 4; (b) CPZDA 4 loaded with Ni.

The IR spectrum of HCDAP **6** (Figure 4.6a), shows the presence of C=O of COOH symmetric and antisymmetric stretching of COO^- at 1467 and 1645 cm^{-1} respectively. The C-N absorption appears at around ~1467 cm^{-1}. Looking at IR spectrum of the resin after loading with cobalt (Figure 4.6b) displayed the increase in the intensity together with broadening of the phosphonate P-O vibrations due to adsorption of the metal [90]. The new absorption band at 1383 cm^{-1} is that of ionic nitrate group by the fact that, the adsorption studies were performed in the presence of nitrates [91]. In the unloaded HCDAP 6, the C=O stretch shift dramatically to 1645.8 cm^{-1} and 1467.1 cm^{-1} for asymmetric and symmetric vibrations respectively because it is now in COO^- form (figure 4.2b).

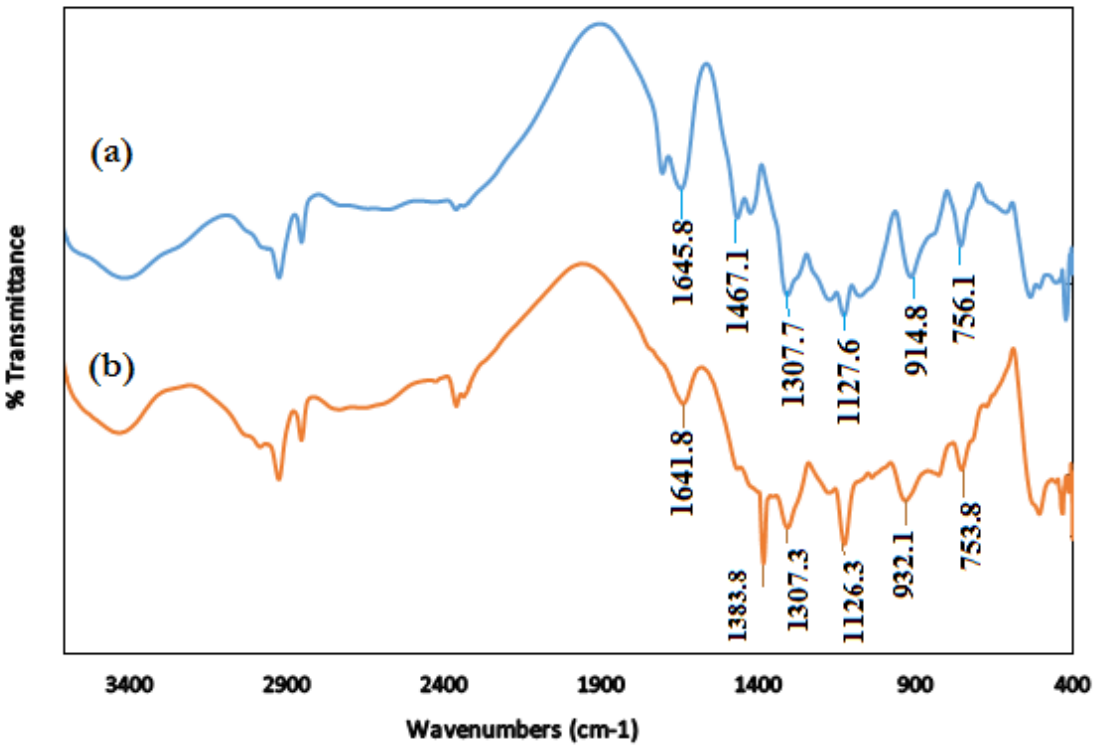


Figure 4. 6 IR Spectra of cross-linked resins (a) HCDAP (b) HCDAP loaded with Cobalt

In Fig. 4.7 FT-IR spectra of the HCPZA shown alone and after the adsorption of Cr. 3442.1 and 3230.58 cm^{-1} bands correspond to –OH stretching vibrations. The peaks at 2925.6 and 2853.9 cm^{-1} indicate –C–H stretch of alkane functional group while peak at 1733.6 cm^{-1} indicates carboxyl group (–C=O) stretching in while the band at 1618.60 cm^{-1} was attributed to –C=O vibrations in the alkenes together with aromatic functional groups. For peaks 1097 and 1382 cm^{-1} correspond to –C=O stretching. At the end of adsorption, peak at 3440.8 cm^{-1} shifted to higher wavelength of 3442.1 cm^{-1} shows that –OH groups of HCPZA play a role in the adsorption. As the 400–1000 cm^{-1} region, there were no major shifts observed.

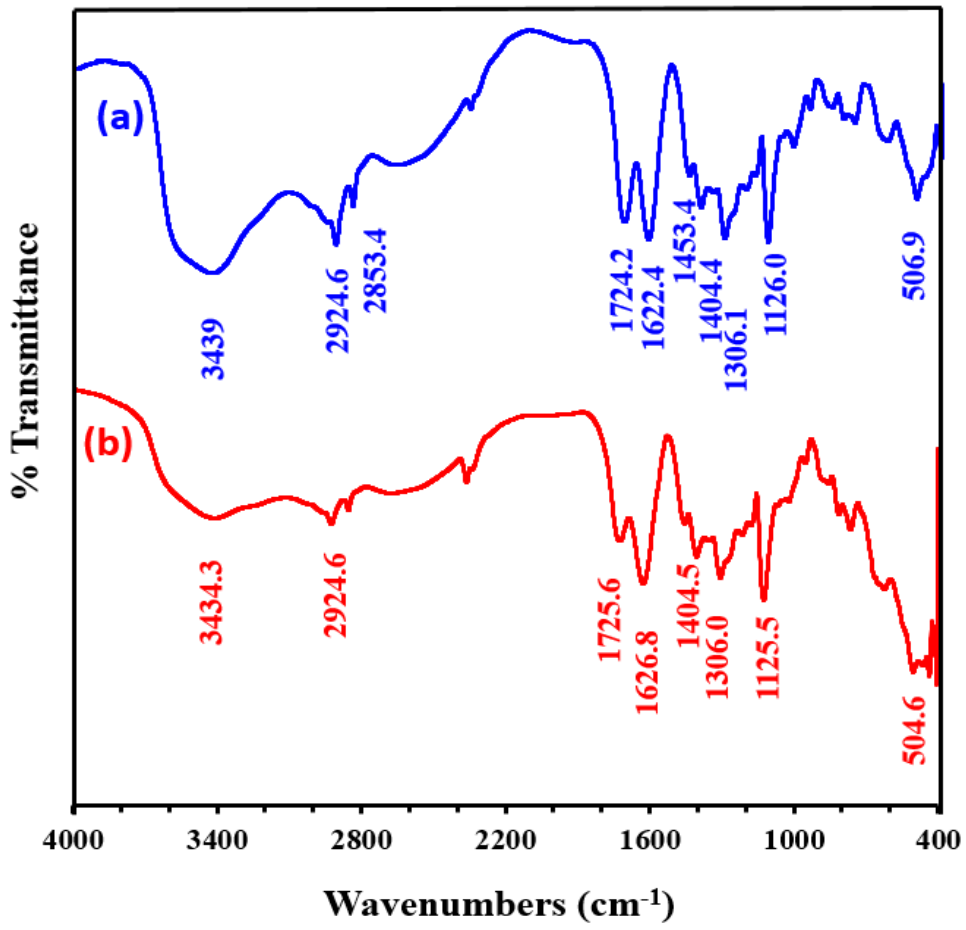


Figure 4. 7 IR Spectra of cross-linked resins (a) HCPZA (b) HCPZA loaded with Chromium

4.2.4 Zeta potential Measurement

The zeta potentials of the cross-linked polymers are shown in Fig. 4.6, 4.7 and 4.8. It was observed that **CPZDA, HCDAP and HCZPA** had negative zeta potentials in basic solutions, from electrostatic angle, the negative charge under the condition would favor the adsorption of positively charged species. Which in our own case are the metals ions. The various functionalities on the polymers may be the key to the negative zeta potential.

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -8.01	Peak 1:	-8.01	100.0	5.75
Zeta Deviation (mV): 5.75	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.0122	Peak 3:	0.00	0.0	0.00

Result quality : Good

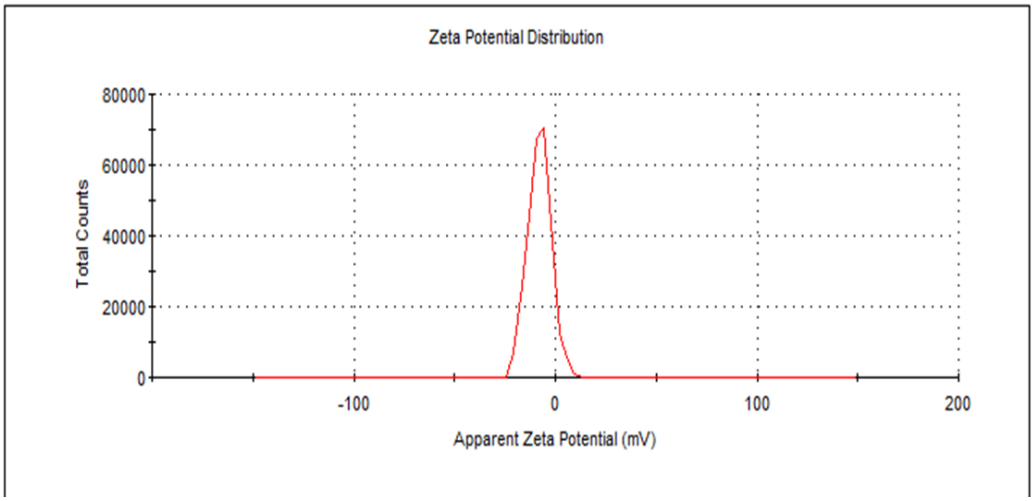


Figure 4. 8 Zeta potential graph of HCDAP

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -6.51	Peak 1:	-10.1	94.8	8.44
Zeta Deviation (mV): 50.6	Peak 2:	113	1.9	4.60
Conductivity (mS/cm): 0.00272	Peak 3:	43.6	1.2	4.78

Result quality : See result quality report

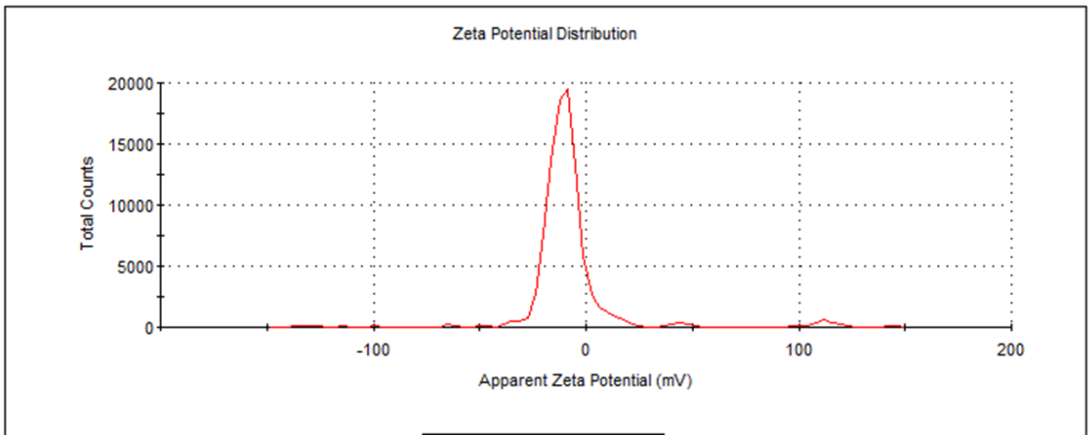


Figure 4. 9 Zeta potential graph of CPZDA

		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): 1.39	Peak 1:	1.39	100.0	6.74
Zeta Deviation (mV): 6.74	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.0891	Peak 3:	0.00	0.0	0.00

Result quality : See result quality report

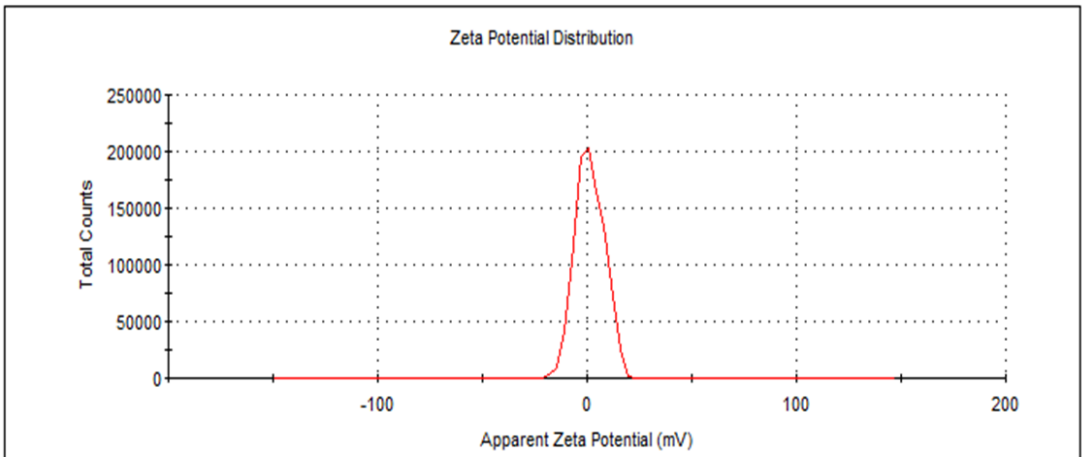


Figure 4. 10 Zeta potential graph of HCPZA

4.2.5 Scanning Electron Microscopy

A scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis were performed to examine the surface morphology and the structure of the resin before and after adsorption.

Figure 4.9 a and b. In the EDX spectrum of the Nickel-loaded resin, adsorption of Nickel is indicated by the characteristic peaks for Ni (II) at 5.4 and 0.57 keV in addition to the peaks of the other elements constituting the resin. The inset tables in Fig. 8 present the apparent concentration and the elemental weight percent's of all the elements present in the loaded and unloaded resin.

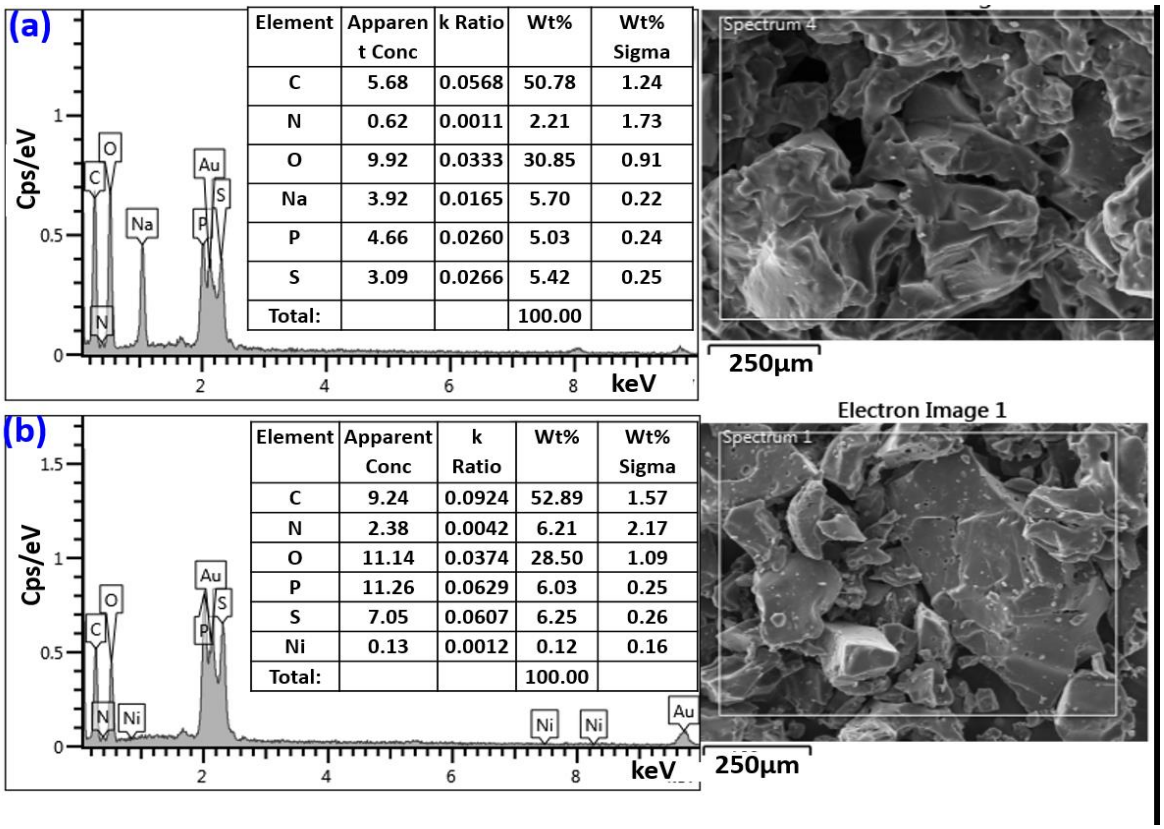


Figure 4. 11 . EDX spectrum and the corresponding SEM image with a table of quantitative microanalysis of the (a)CPZDA; (b) Nickel-loaded resin

Figure 5.1 a and b. In the EDX spectrum of the Cobalt-loaded and unloaded resin, adsorption of Cobalt is indicated by the characteristic peaks for Co (II) at 6.9 and 0.7 keV in addition to the peaks of the other elements constituting the resin. The table in Figure 5.1 a and b present the apparent concentration and the elemental weight percent's of all the elements present in the loaded and unloaded resin.

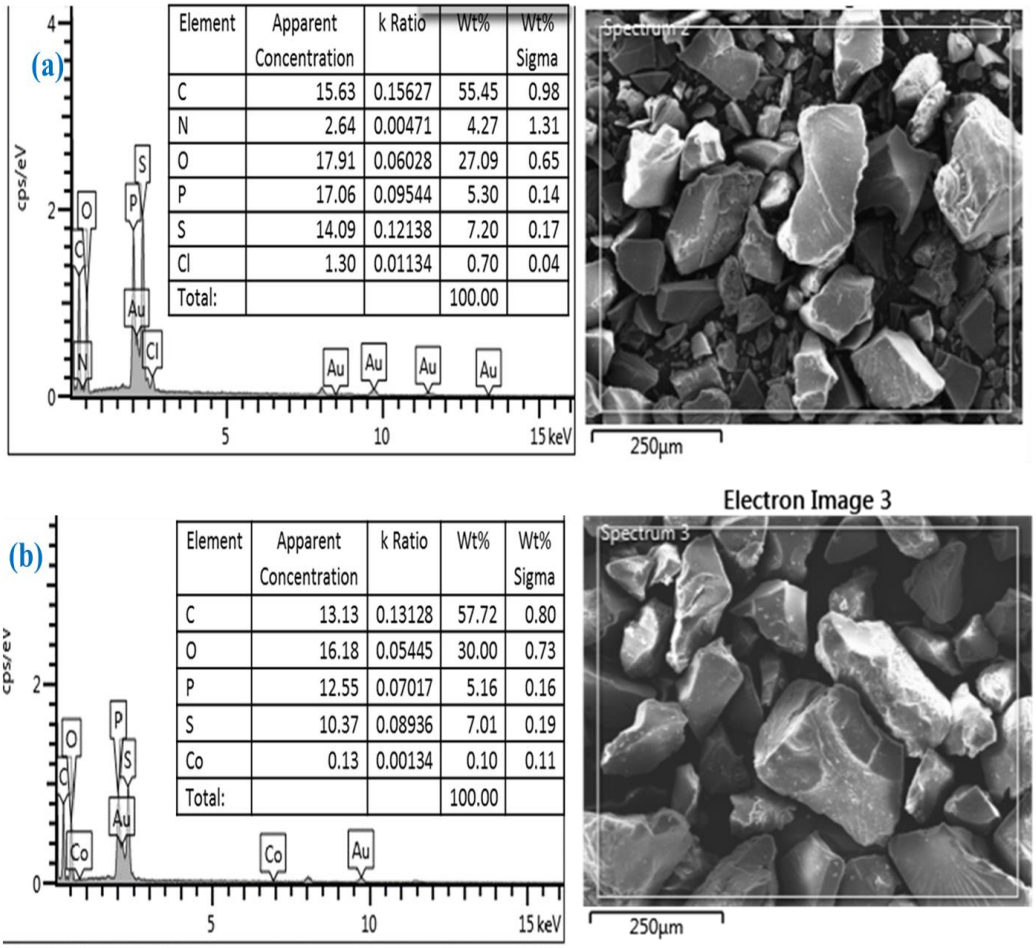


Figure 4. 12 EDX spectrum and the corresponding SEM image with a table of quantitative microanalysis of the (a) HCDAP; (b) Cobalt-loaded resin

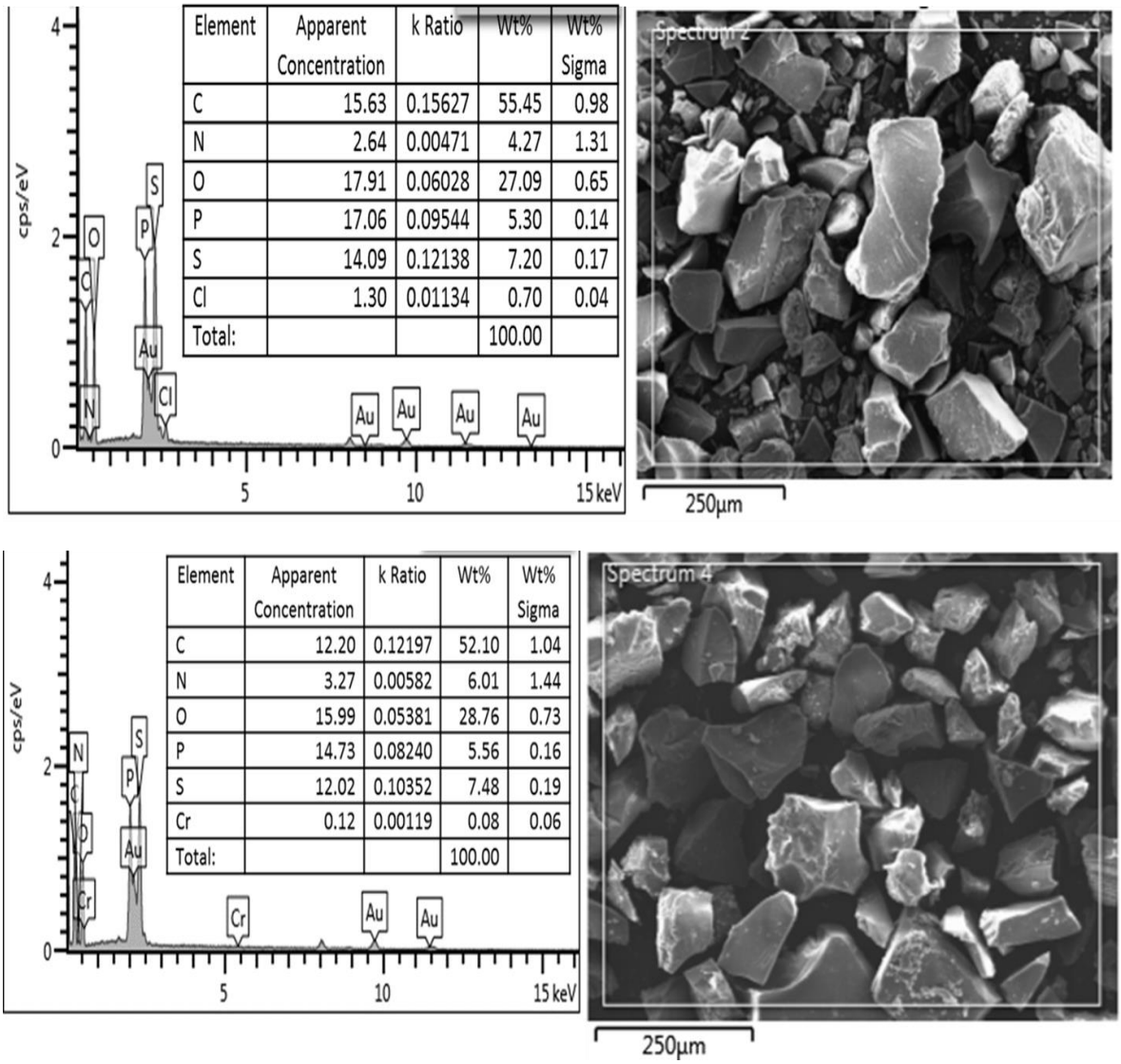


Figure 4. 13 EDX spectrum and the corresponding SEM image with a table of quantitative microanalysis of the (a) HCDAP; (b) Chromium-loaded resin

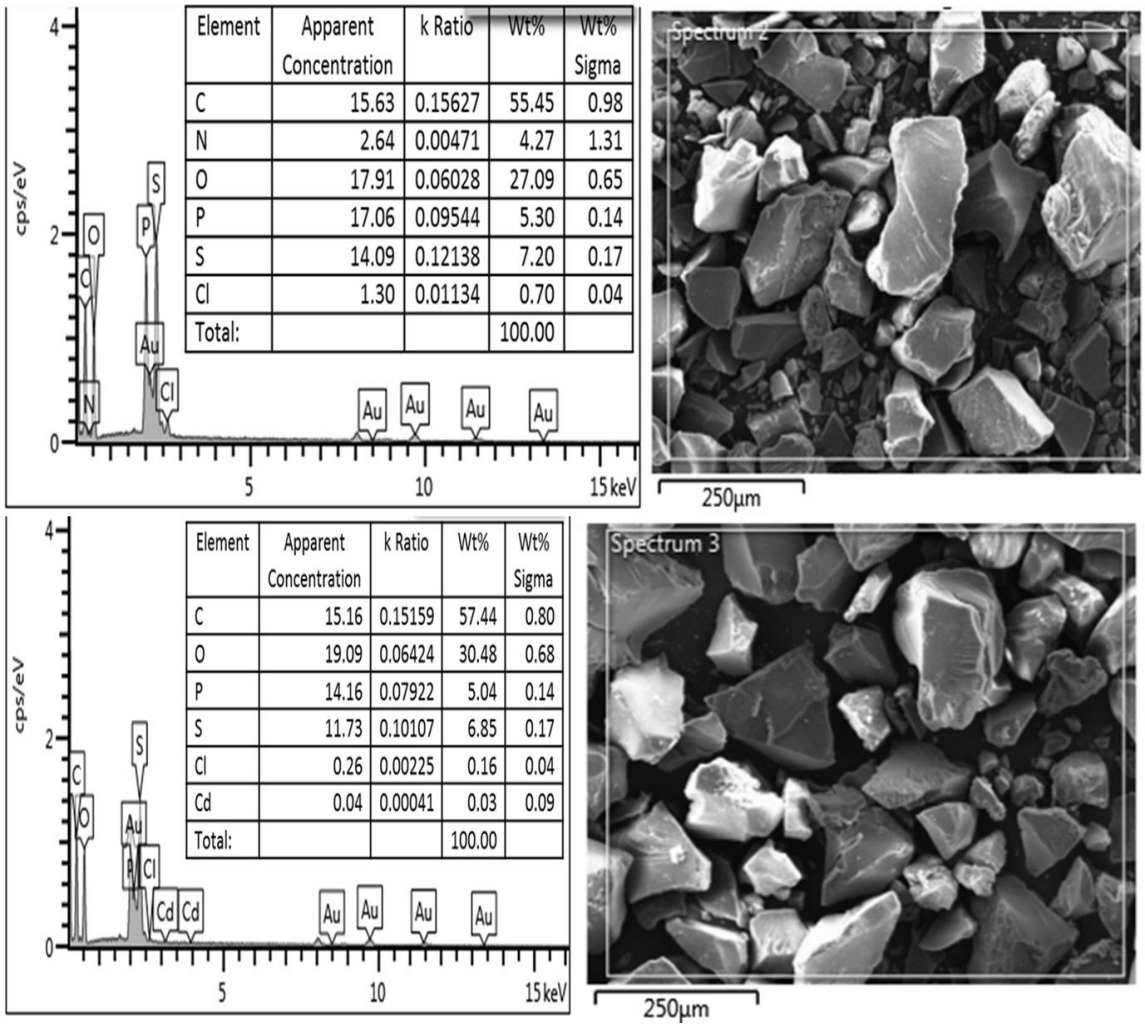


Figure 4. 14 EDX spectrum and the corresponding SEM image with a table of quantitative microanalysis of the (a) HCDAP; (b) Cadmium-loaded resin

4.3 Sorption Evaluation

4.3.1 pH Effect

pH medium of the initial Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+} solutions plays a vital role during the removal of the species by organic-adsorbents, similar to those under consideration. As a pH dependent polymer, knowing the pH of the solution is considered vital in adsorption [92-94]. Therefore, pH of the initial solutions was varied within the range of 3-7. Studies at pH > 7 were not executed to avoid metal ion precipitation. The maximum % removal was achieved at a range of pH 5–7, Figure 4.15a shows the amount of metal adsorbed and the adsorption percentage of Co (II), Cd (II), Ni (II) and Cr (III) versus initial solution pH. Initially, as the pH of solution was increased from 3-5, the removal percentage of Co (II), Ni(II), Cd(II) and Cr(III) increased respectively from 17.4 to 50%, from 19 to 78%, from 5 to 22 % and from 5 to 10%. All of these species are positively charged which make them attractive to the negatively charged active motifs on the polymer chain, and thus get them adsorbed on the polymer. The low adsorption at pH 3.0 could be justified by the high competition between the excess protons H^+ which can compete with the metal ions, resulting in a lower adsorption. The uptake increase with increasing pH. This could be defined by any significant H_3O^+ versus M^{n+} competitive-adsorption on the active sites. At pH > 7, the removal can be accomplished by concomitant precipitation and sorption. Therefore, in the present study, pH 3-7 was chosen for the experiments to avoid the precipitation of the nickel in agreement to [95]. Influence of various functional groups (acidic or basic) can lead to both protonation and deprotonation. The maximum % removal was achieved at a range of pH 5.5 for Nickel (II), pH 6 for Cobalt (II), pH 5 for chromium while the pH has no significant influence on Cadmium

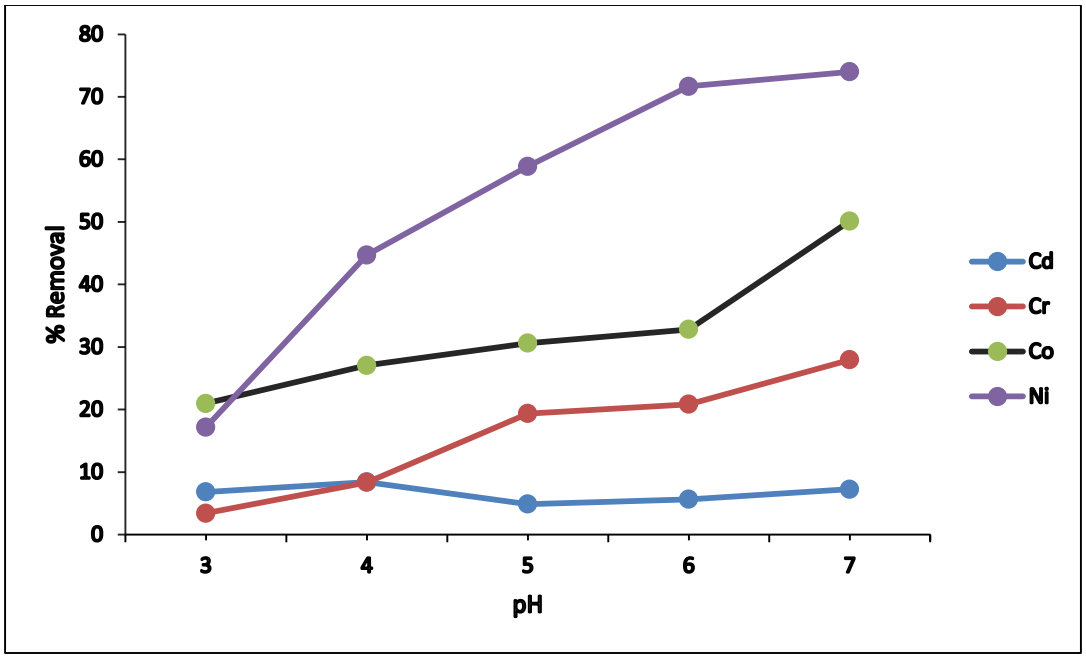


Figure 4. 15a The influence of medium pH on the adsorption of behavior Co (II), Ni(II), Cd(II) and Cr(III on HCDAP (30mg adsorbent, pH= 6 and initial concentration of 10ppm)

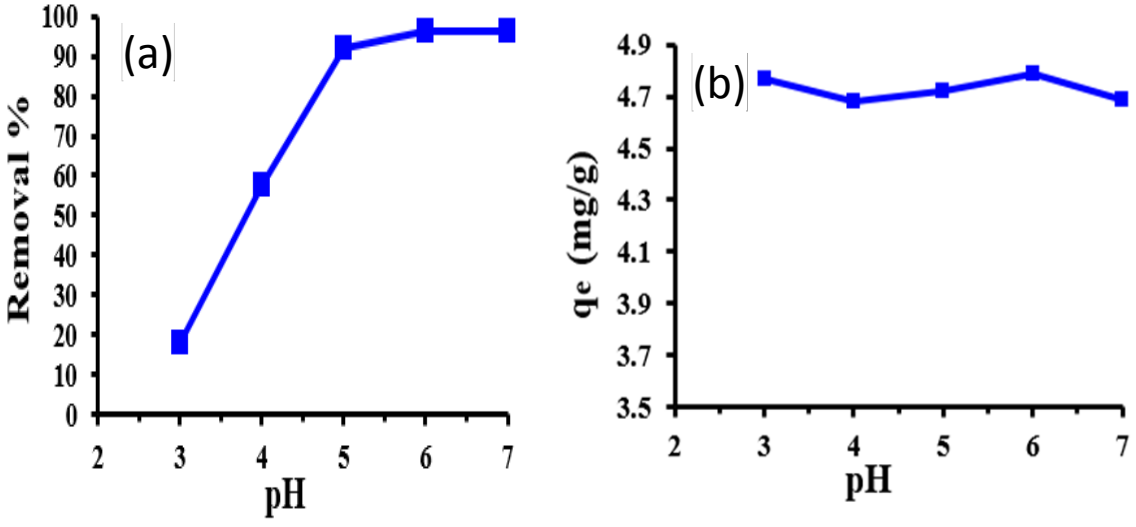


Figure 4. 16b The influence of medium pH on the adsorption of behavior (a) Ni (II) on CPZDA (b) Cobalt (II) on HCDAP

4.3.2 Role of contact time and initial concentration

The influence of contact time was investigated by adopting batch experiments with initial concentrations of 5, 10, and 20 ppm. The experiments for the contact time were performed at 24ºC. Initially, the availability of the active motifs and uncovered surface of the polymer accounted for rapid of Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^{2+}species adsorption. The adsorption was favored by increased contact time up to around 60 minutes, corresponding to equilibrium point. After that, increasing the contact time has no considerable enhancement on the adsorption percentage. Lower binding capacity of Cd (II) ions over the other metals ion on the polymer could be explained by various complex chemistry that might play out. Comparing the hydration radius and Pauling′s electronegativity of Cd (II) ions as compare to the others. Generally, at the same experimental conditions, the adsorption data show an affinity for Ni (II) ion. The removal of heavy metals in this study were in the order of Ni(II)>Co(II)>Cr(III)>Cd(II), which coincide reasonably well with the reversed order trend of hydrated radius with the exception of Cr (III) as Cd(II) (4.26 Å)>Co(II) (4.23 Å)>Cr(II) (4.61 Å)>Ni(II) (4.04 Å) and Pauling′s electronegativity (Ni(II) (1.91)>Cr(III) (1.90)>Co(II) (1.88)>Cd(II) (1.69) [96]. The smaller the ionic radius and the greater the valence, the more closely and strongly is the heavy metal ions adsorbed, thereby, the greater ion′s hydration, the farther it is from the hydroxide surface and the weaker its removal. The hydration radius of Ni (II) was the smallest, so its removal was the highest. Likewise, the hydration radius of Cd (II) was the biggest, was the bigger and react, so its removal was the lower. Also there might be selectivity by the polymer for a particular metal ion.

For Co (II) species adsorption (see Fig.4.17), the adsorption was favored by increased contact time up to around 60 minutes, corresponding to equilibrium point. After that, increasing the contact time has no considerable enhancement on the adsorption percentage.

4.3.2.1 Effect of Adsorbent dosage

The effect of adsorbent dose on the removal percentage (R%) of Cd^{2+}, Co^{2+}, Cr^{3+} and Ni^{2+} was studied and is shown in Figure (4.15b). As the dose was increased from 10 to 50 mg. the percentage of adsorbed metal ions increased from 10 % to 82 %, whereas the adsorption capacity decreases from 12.18 to 2.55 mg g-1. Above 50 mg of adsorbent dose, there was no significant increase in the removal, but the adsorption capacity decreased rapidly. Considering percentage removal (%) adsorbent dose of 30mg was found to be the optimum dose and was used for all other experiments. This was all noticed for all the polymers used in the study.

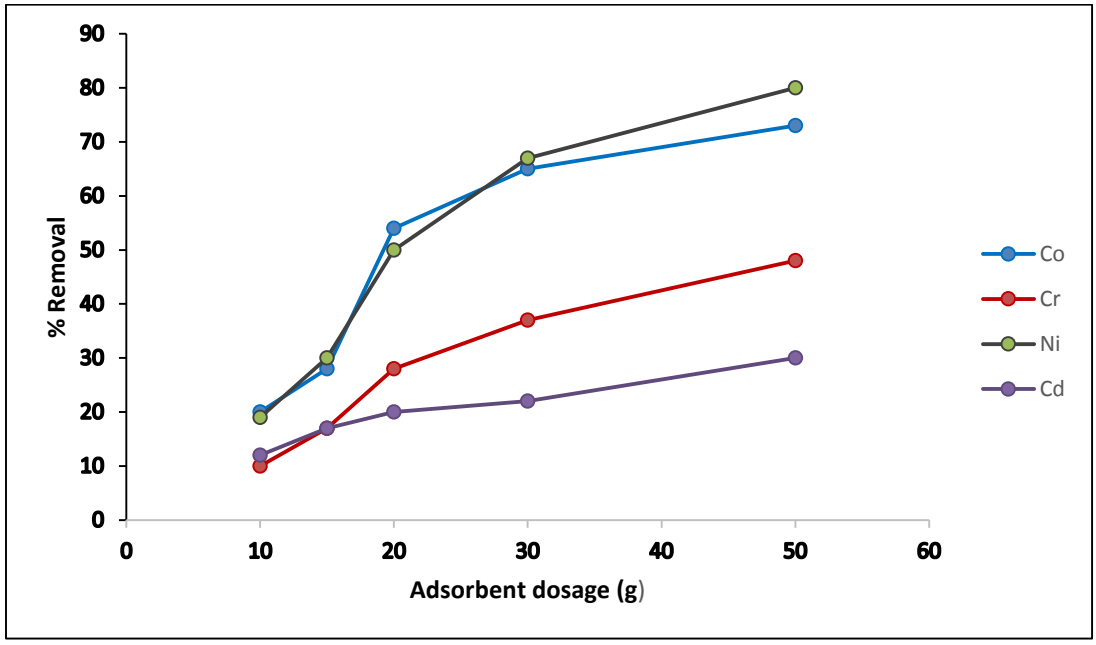


Figure (4.15b). Determination of the optimal dose of CPZDA (C_0 = 50 mg; initial pH 6; T= 22°C; t = 2h).

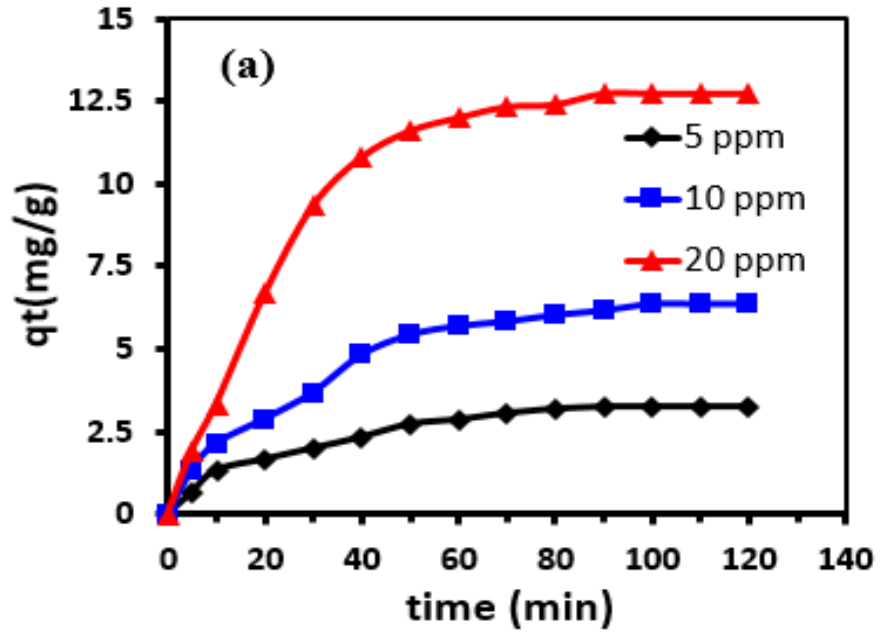
4.3.3 Kinetics of the adsorption

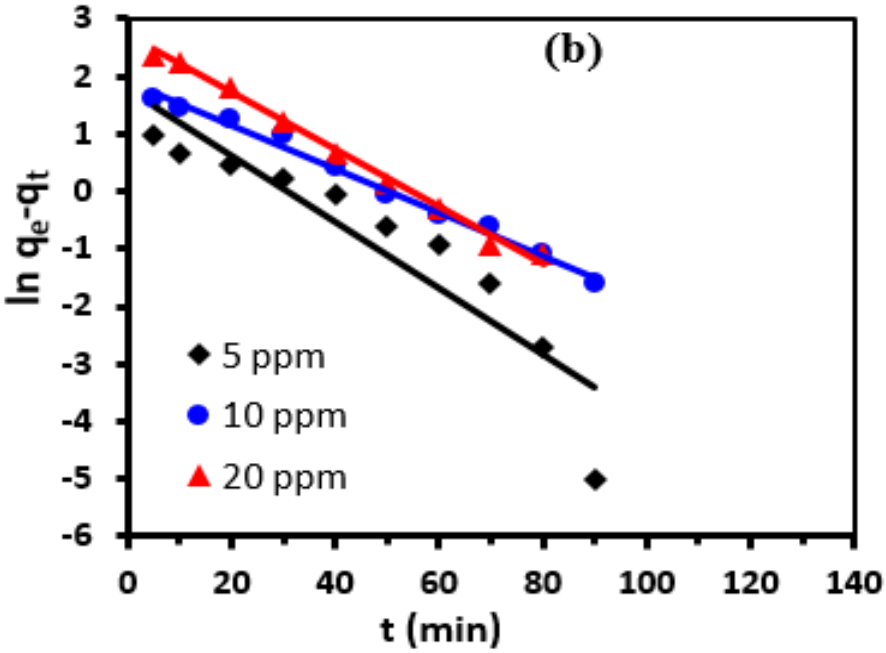
Monitoring the interaction of the polymer with Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+} species kinetically can provide valuable data for understanding the mechanism of the adsorption. Here, two models (Lagergren's pseudo-first and second orders) are the common models adopted for adsorption studies with metals and were therefore considered in this case.

Equation for Lagergren's pseudo-first order kinetics is presented by [97]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

Where q_t and q_e stand for the amounts of Cd^{2+}, Co^{2+}, Cr^{3+} or Ni^2 (mg/g) adsorbed at any time *t* and at equilibrium respectively with k_1 stands for the rate constant of the first order (min^{-1}). The values of k_1 and adsorption density q_e are obtained from the plots of ln (q_e - q_t) versus *t* (Fig. 5.5b) and presented in Table 4.2. Comparing the experimental value observed for equilibrium adsorption ($q_{e, exp}$) with the one computed theoretically ($q_{e, cal}$), it is clear that there is no agreement between the values. The obtained correlation coefficients (R^2) for the first model show poor linearity for Ni (II). This assumes that the adsorption deviates from the Lagergren's pseudo-first model.


(a)
qt(mg/g)
time (min)
5 ppm
10 ppm
20 ppm
0
2.5
5
7.5
10
12.5
15
0
20
40
60
80
100
120
140


(b)
ln qe-qt
t (min)
5 ppm
10 ppm
20 ppm
3
2
1
0
-1
-2
-3
-4
-5
-6
0
20
40
60
80
100
120
140

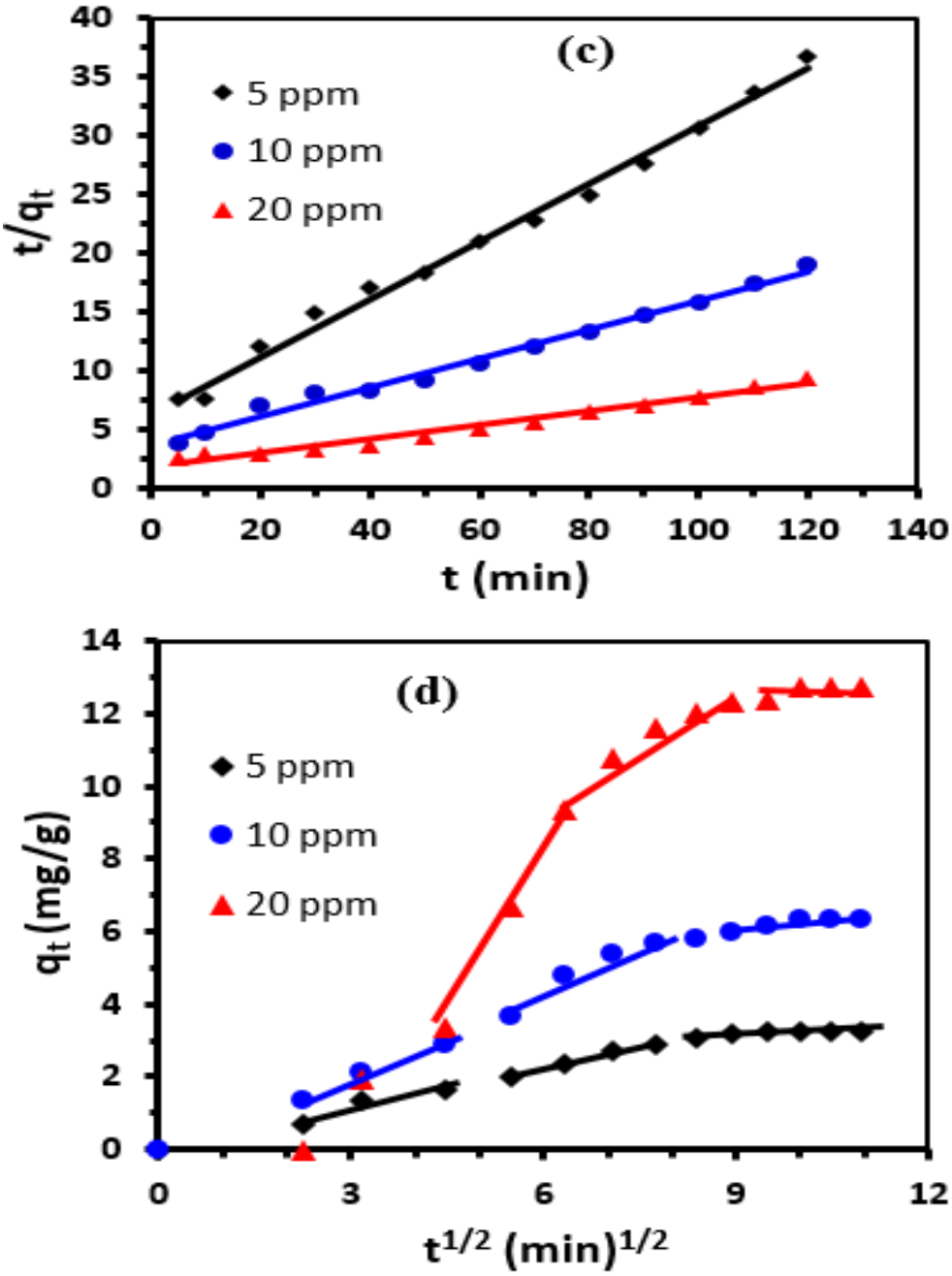


Figure 4. 17 Variation of qt with contact time (a); Lagergren's pseudo-first order (b); Pseudo-second-order (c); Intraparticle diffusion (d), plots for Ni (II) adsorption on CPZDA at various initial concentrations at pH 5.5, 23^{o}C and shaker agitation speed of 150 rpm

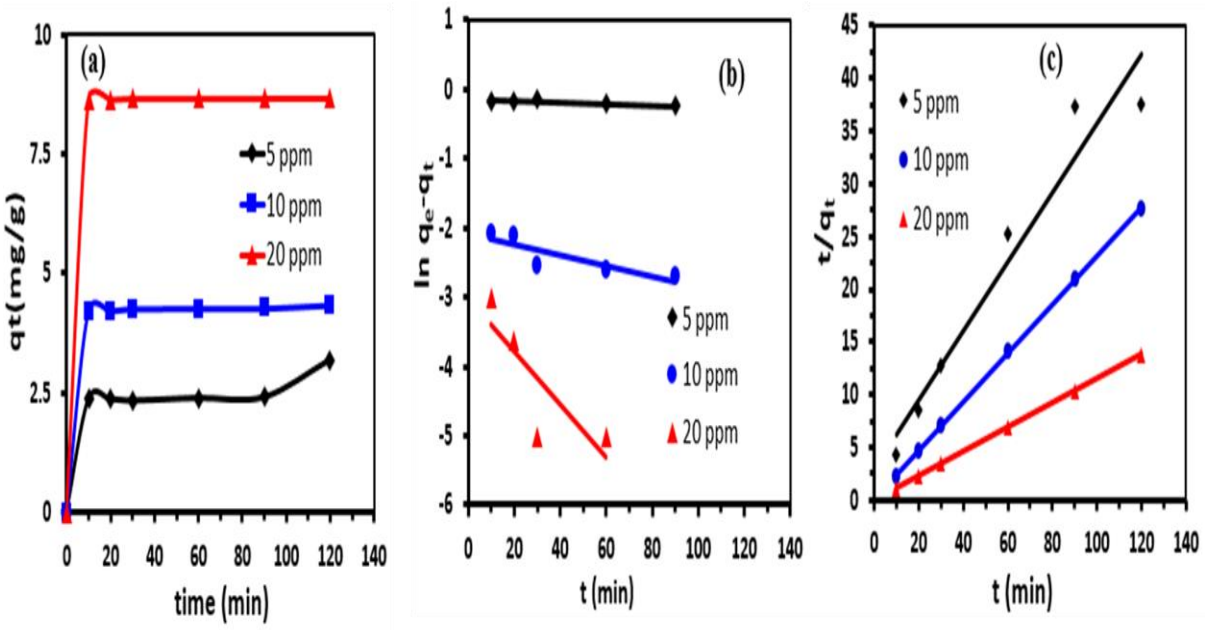


Figure 4. 18 (a) q_t with contact time for the removal of Co(II) by the polymer for different feed concentrations; (b) Lagergren's pseudo-first order; (c) Pseudo-second-order.

The following adsorption kinetic rate equation is used to express the pseudo-second order kinetic model [98, 99]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

k_2 depicted the rate constant of the pseudo-second order adsorption (g/mg.min), q_e and q_t are the adsorbed amount (capacity) of Co (II) at equilibrium and at time t.

In linear form, the pseudo-second order can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

Where k_2, the rate constant (g/mg.min) is obtained by a plot of t/q_t against t (Fig. 5.5c). All the kinetic parameters are listed in Table 4.2. The initial adsorption rate is h= $k_2 q_e^2$ (mg/g.min).

The values of the correlation coefficients (R^2 >0.99) for all the concentrations fitted the proposed model and the interaction could be described as chemically-mediated. Therefore, consistency can be assumed for the equilibrium adsorption capacities ($q_{e,\ cal}$) with the experimentally observed data ($q_{e,\ exp}$), Table 4.2. These findings fitted well with earlier investigations using similar ions and organic-adsorbents [100-102].

4.3.3.1 Intraparticle diffusional model

An important approach for following the adsorption mechanism is by monitoring intraparticle diffusional properties. Plotting q_t on y-axis against $t^{1/2}$ becomes linear when

the mechanism of the adsorption follows the intraparticle diffusion where the adsorbate ions diffuse in the intraparticle pore of the adsorbent. However, more than one step could govern the process if the data takes a multi-linear plots. Intraparticle diffusion co-efficient, k_{id}, can be determined by fitting the data from the experiment in the intraparticle diffusion model [103, 104] expressed:

$$q_t = k_{id} t^{1/2} + C \qquad (7)$$

where k_{id} is the intraparticle diffusion rate constant (mg/g.min^{½}), C is the intercept (mg/g). Our experimental data, Fig. 5c, revealed that the plot of q_t versus $t^{1/2}$ is multi-linear, indicating that three steps are involved in the process (adsorption) and intraparticle diffusion is not the only rate-limiting step [105, 106]. It is observed that, there are three linear portions that explain the adsorption stages; these are the external mass transfer at initial period, intraparticle diffusion of Co (II) on the resin, and adsorption on the interior sites. The intraparticle diffusion constant values are shown in Table 4.3.

Table 4. 2 Kinetic constant parameters obtained for Ni (II) adsorption on CPZDA

C_i (mg/L)	q_e, exp (mg/g)		Lagergren's pseudo-first order				Pseudo-second order				Intraparticle diffusion model		
			k_1 (min^{-1})	q_e, cal (mg/g)	R^2		k_2[a]	q_e, cal (mg/g)	R^2		k_{id}[b]	C (mg/g)	R^2
5	3.27		0.0574	5.75	0.850		0.0095	4.08	0.992		0.62	0.19	0.990
10	6.33		0.0379	8.17	0.941		0.0038	8.15	0.991		0.92	2.9	0.999
20	12.73		0.1152	43.80	0.960		0.0022	16.72	0.956		0.70	3.5	0.950

[a](g/mg.min). [b](mg/g.min)

Table 4. 3 Kinetic constant parameters obtained for Co (II) adsorption on HCDAP

			Lagergren's pseudo-first order				Pseudo-second order				Intraparticle diffusion model		
C_i (mg/L)	q_e, exp (mg/g)		k_1 (min^{-1})	q_e, cal (mg/g)	R^2		k_2[a]	q_e, cal (mg/g)	R^2		k_{id}[b]	C (mg/g)	R^2
5	3.19		0.001	0.85	0.623		0.0375	3.04	0.958		0.68	0.187	0.999
10	4.33		0.007	0.12	0.762		0.385	4.33	0.999		0.85	2.89	0.988
20	8.67		0.038	0.05	0.685		1.899	8.63	0.999		0.62	3.5	0.996

[a](g/mg.min). [b](mg/g.min)

4.3.3.2 Isotherms of the adsorption

Isotherms provide fundamental physiochemical data to evaluate sorption capacity. Here in the present study, three isotherms were employed to analyze the experimental results.

Langmuir Isotherm Model: Langmuir introduces a concept of forming a single (monolayer) surface phase (a monomolecular adsorption) on energetically homogeneous surfaces of the adsorbent. Thus, the Langmuir equation describes a physical or chemical adsorption on solid surfaces [105-107]. This is called ideal localized monolayer model.

The linear Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \qquad (8)$$

Where k_L is Langmuir equilibrium constant (litres/milligrams) related to the affinity of adsorption sites, and q_m (mg/g) is the maximum theoretical monolayer adsorption capacity, Ce is the equilibrium concentration (mg/L) of Co (II) in solution and q_e is the amount Cobalt ions adsorbed (mg/g) at equilibrium. Figure 5.6a depicts the plot of C_e/q_e versus C_e.

The values of Langmuir constants q_m and k_L were computed from the slope and intercept of the plot, and are given in Table 4.4. From the data, the adsorption capacity q_m was determined by linear Langmuir equation to be 76.9 mg/g of Co (II), k_L of 0.02 L/mg and the R^2 value of 0.86, proving that the data fitted the Langmuir Isotherm model.

The characteristic parameter of the Langmuir isotherm is illustrated in terms of dimensionless equilibrium parameter R_L, also known as separation factor, defined by Weber and Chakkravorti [99]:

$$R_L = \frac{1}{1 + K_L C_o} \qquad (9)$$

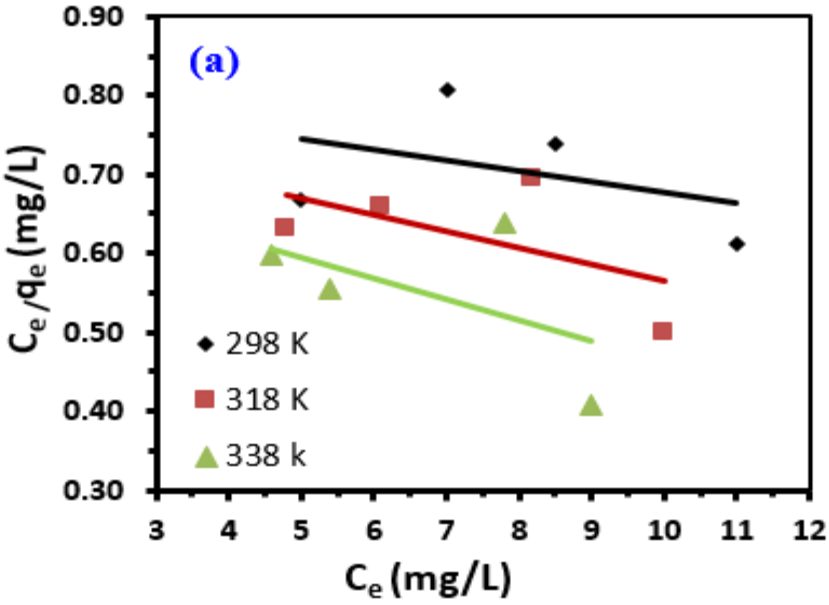
Where C_o is the initial solute concentration. The value R_L gives an indication of the type of the isotherm and the nature of the adsorption process. It indicates whether the adsorption nature is either unfavourable (R_L>1), linear (RL =1), favourable (0< R_L<1) or irreversible (R_L = 0). From the data calculated and presented in Table 4.4, the R_L of 0.14 indicates the favourable nature of the adsorption. The maximum adsorption capacities from the Langmuir isotherm of the present adsorbent for the removal of Co (II) was compared with those of other adsorbents reported in the literature, Table 3. Interestingly, the adsorption capacity of the present resin is higher than those of the other sorbents. The values of Langmuir constants q_m and k_L were computed from the slope and intercept of the plot, and are given in Table 4.5. From the data, the adsorption capacity q_m was determined by linear Langmuir equation to be 45.5 mg/g of Ni(II), k_L of 0.34 L/mg and the R^2 value of 0.99, proving that the data fitted the Langmuir Isotherm model.

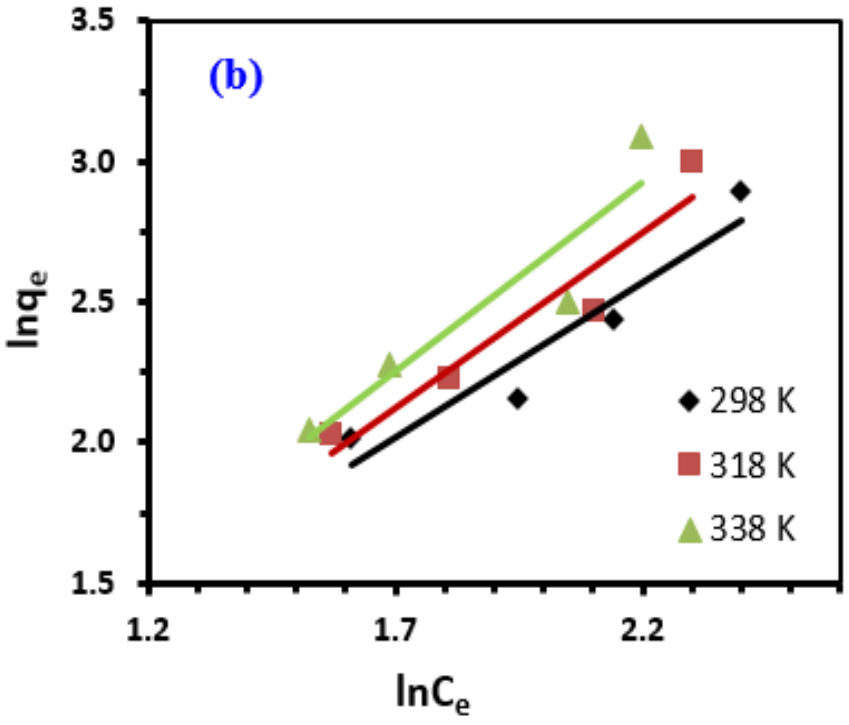
Table 4. 4 Langmuir, Freundlich and Temkin isotherms constants for Co (II) adsorption on HCDAP

	Langmuir isotherm				Freundlich isotherm				Temkin isotherm		
T (K)	q_m	k_L	R_L	R^2	1/n	n	k_f	R^2	K_T	b_T	R^2
298	76.9	0.02	0.14	0.1502	1.11	0.90	1.147	0.9594	3.146	0.191	0.8464
318	47.6	0.03	0.21	0.3220	1.24	0.81	1.025	0.9429	3.174	0.162	0.8293
338	38	0.04	0.23	0.2898	1.34	0.75	1.022	0.9385	3.128	0.139	0.7725

Table 4. 5 Langmuir, Freundlich and Temkin isotherms constants for Ni(II) adsorption on CPZDA

	Langmuir isotherm				Freundlich isotherm				Temkin isotherm		
T (K)	q_m (mg/g)	k_L	R_L	R^2	1/n	n	k_f (mg/g)	R^2	K_T	b_T	R^2
296	45.5	0.40	0.34	0.999	0.55	1.82	12.68	0.991	3.78	0.248	0.978
316	46.7	0.62	0.38	0.989	0.49	2.04	15.64	0.977	5.11	0.234	0.992
336	50.8	0.74	0.64	0.995	0.46	2.17	19.88	0.988	7.08	0.218	0.990


(a)
0.90
0.80
0.70
0.60
0.50
0.40
0.30
C_e/q_e (mg/L)
298 K
318 K
338 k
3
4
5
6
7
8
9
10
11
12
C_e (mg/L)


(b)
3.5
3.0
2.5
2.0
1.5
$\ln q_e$
298 K
318 K
338 K
1.2
1.7
2.2
$\ln C_e$

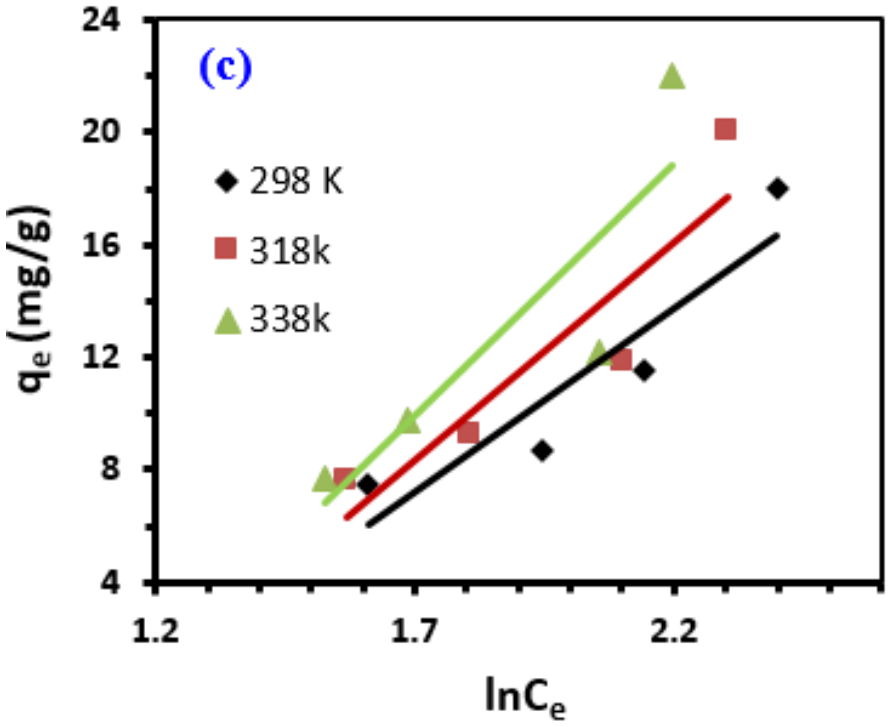
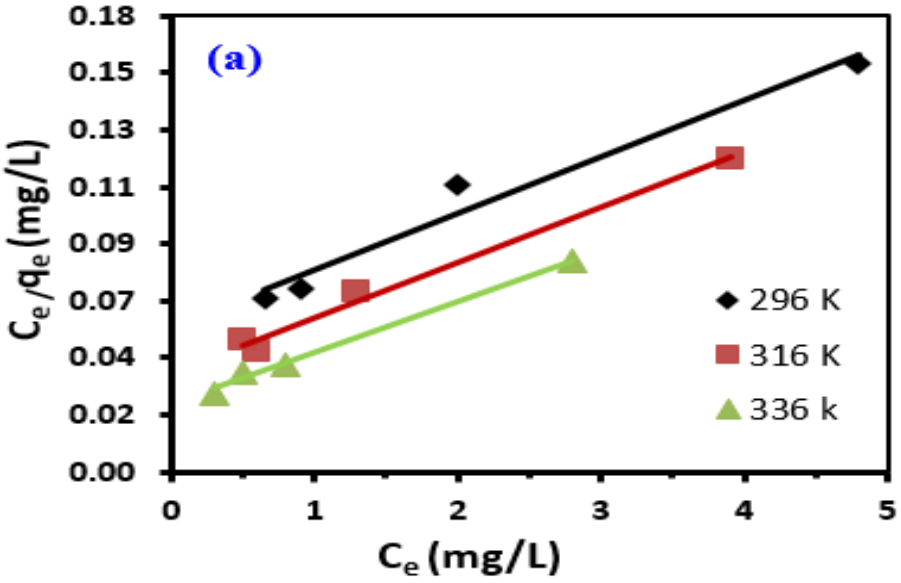
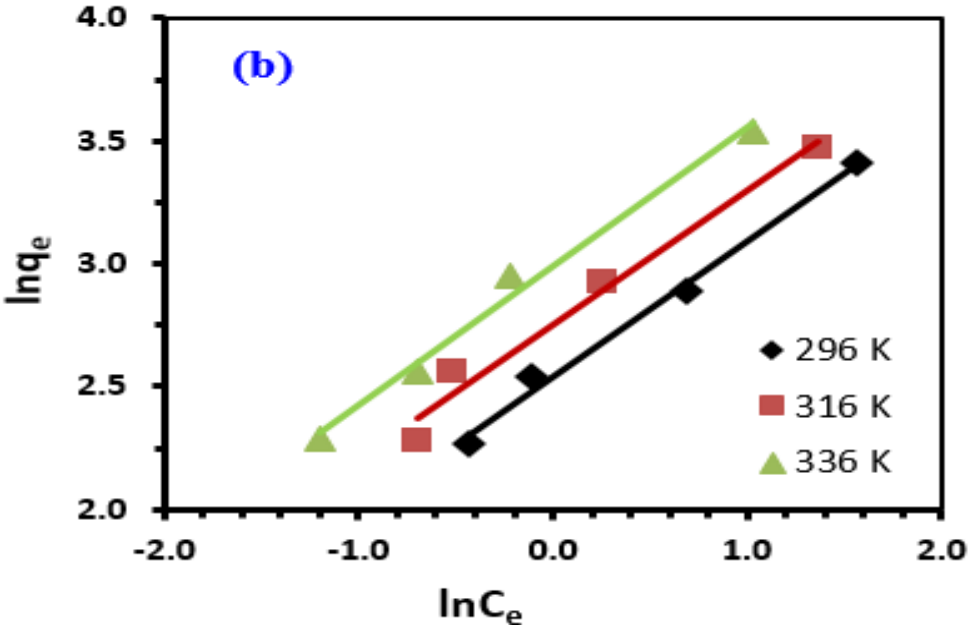


Figure 4. 19 Langmuir (a) Freundlich (b), and Temkin (c) adsorption isotherms for Co (II) adsorption on HCDAP at initial concentration of 20 ppm and different resin dosages.


(a)
0.18
0.15
0.13
0.11
0.09
0.07
0.04
0.02
0.00
0
1
2
3
4
5
C_e/q_e (mg/L)
C_e (mg/L)
296 K
316 K
336 k


(b)
4.0
3.5
3.0
2.5
2.0
-2.0
-1.0
0.0
1.0
2.0
lnq_e
lnC_e
296 K
316 K
336 K

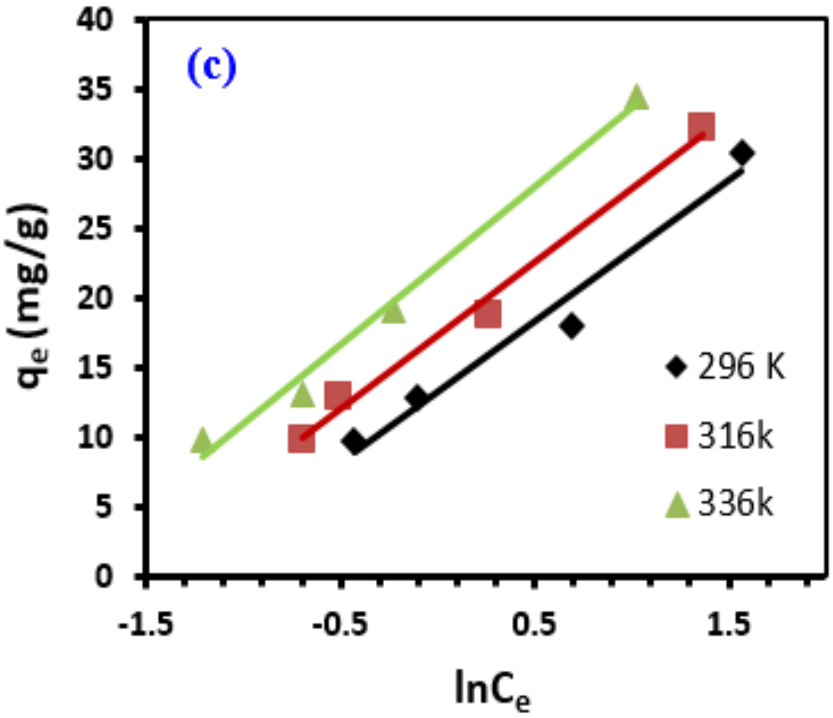


Figure 4. 20 Langmuir (a) Freundlich (b), and Temkin (c) adsorption isotherms for Ni(II) adsorption on CPZDA at initial concentration of 40 ppm and different resin dosages

4.3.3.3 Freundlich Isotherm Model

Freundlich model describe the sorption characteristics on heterogeneous surfaces taking into account the interactions between the adsorbed molecules [48]. The following empirical equation is used:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (10)$$

Where k_F (mg/g) accounts for the Freundlich isotherm constant indicating adsorption capacity and n stands for adsorption intensity while 1/n is a function of the strength of the adsorption, C_e is the equilibrium concentration of adsorbate (mg/L) and q_e is the amount of adsorbate per adsorbent at equilibrium (mg/g). The logarithmic form of Freundlich is defined as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (11)$$

From the plot of Ln q_e versus Ln C_e, Fig. 5.86b, K_F and n were calculated, Table 2. The *n* value predicts the feasibility of the adsorption process. The value of n > 1 represents a favourable adsorption. A value of 1/n <1 indicates a normal adsorption while 1/n>1 indicates a cooperative adsorption. Therefore, 1/n value of 0.3 obtained could be attributed to a favourable adsorption process of Co(II) on the resin. The value of k_F is 19.8 mg/g and R^2 is 0.95 indicating that the data does not fit this model well.

The Temkin model takes into account the adsorbent–adsorbate interactions and assumes a linear decrease in the energy of adsorption with surface coverage. The Temkin isotherm model is expressed by:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (12)$$

where b_T is the Temkin isotherm constant related to the heat of sorption (joule per mole), k_T is the Temkin isotherm equilibrium binding constant (litres per gram) which is equal to the maximum binding energy (L/g), R is gas constant (8.314×10^{-3} kJ/ mol.K) and T is the absolute temperature (degrees Kelvin). The plot of q_e versus ln C_e is illustrated in Fig. 6c and the isotherm constants were determined. The linear plot for The Temkin adsorption isotherm fits quite well with R^2 of 0.98.

4.3.4 Evaluation of Thermodynamic Variables

Process energetic variables (i.e. $\Delta G^0, \Delta H^0 and \Delta S^0$) were determined in an attempt to assess the overall adsorption process. Experimental results (i.e. Kc values) derived at variable conditions of temperature were employed for the computations. As indicated in equation 13, Van't Hoff approach was adopted by plotting lin Kc on the y-axis against I/T on the x-axis [49, 50]. Therefore, the slope and intercept on y-axis were used to obtain the applicable values of changes in enthalpy and entropy, with which the values of free energy were calculated using equation 14.

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (13)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (14)$$

where R is the gas constant of 8.314 kJ/mol.K, T is the absolute temperature in K, and K_c = q_e/C_e (L/mg) is standard thermodynamic equilibrium constant.

Reduction in the ΔG^0 value as the temperature increase indicates enhanced resin-Co (II) interaction with elevation of temperature. With regards to the positive standard enthalpy change ΔH^o of 23.2 kJ/mol suggests the adsorption of Co (II) on the resin is endothermic and which supported by the trend noticed increasing adsorption of Co (II) with a temperature. The positive standard entropy change of 8.6 kJ/mol. K reflects the affinity of the resin towards Cobalt. It also reveals the increase in randomness at solid-solution interface during the fixation of Co (II) on the active motifs of the resin.

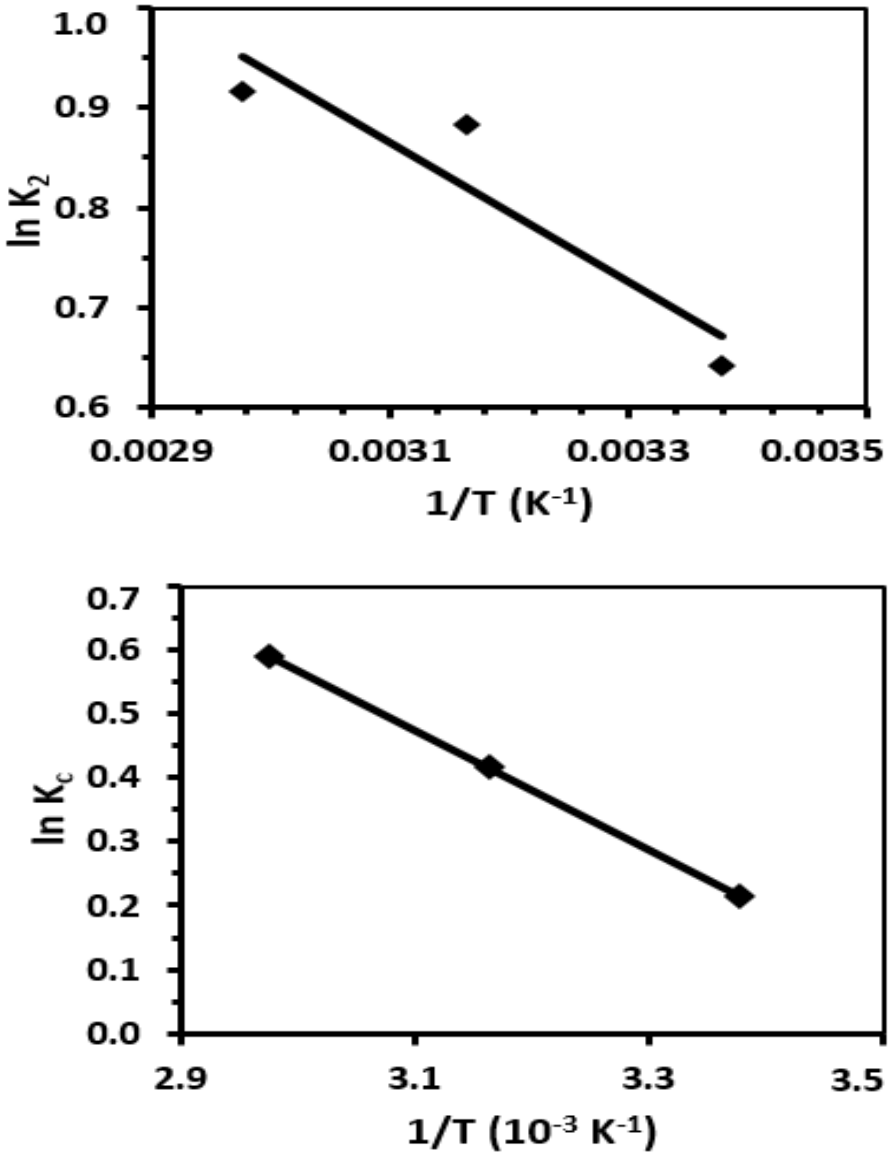


Figure 4. 21 Plot of ln Kc versus 1/T (a) Plot of ln K2 versus 1/T (Arrhenius plot) (b) for Co (II) on HCDAP.

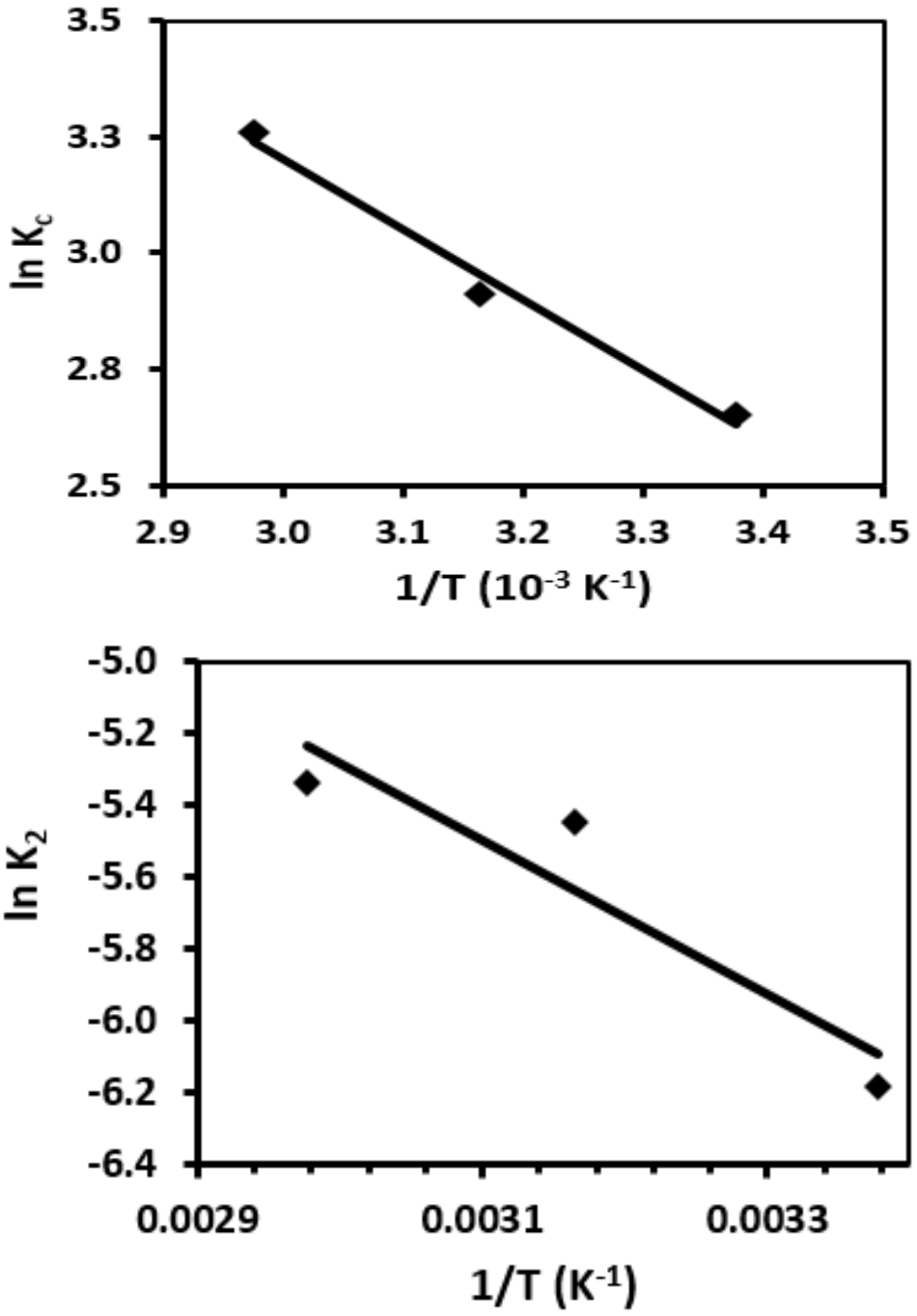


Figure 4. 22 Plot of ln Kc versus 1/T (a) Plot of ln K_2 versus 1/T (Arrhenius plot) (b) for Ni (II) on CPZDA.

Table 4. 6 Thermodynamic parameters for the adsorption of Co (II) HCDAP at different temperatures

T (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol.K)
298	-8.28		
318	-8.82	7.769	2.8
338	-9.41		

Table 4. 7 Thermodynamic parameters for the adsorption of Ni (II) CPZDA at different temperatures

T (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol.K)
296	-2.52		
316	-2.69	23.2	8.6
336	-2.86		

4.3.4.1 Adsorption activation energy

The Ea, which is commonly measured in the units of kJ/mol, represents the minimum energy desired to activate the adsorption process. Equation 15 below was used for its calculations. Plotting a graph of lin K_2 on the y-axis against 1/T on the axis can yield a slope suitable for Ea computation. k_2 and R are the rate and molar gas constant, respectively.

$$\ln k_2 = -\frac{E_a}{R}(\frac{1}{T}) + constant \qquad (15)$$

T is the solution temperature in K. The magnitude of Ea gives an indication of the type of the adsorption process, physical or chemical. Key trend to be considered with Ea is that, the adsorption can be partial (i.e. physisorption, requiring < 40 kJ/mol) or strong interaction by chemisorption. The latter case requires energy that could be up to 800 kJ/mol, depending on the prevailing and applied conditions of the surface and the species involved [100, 108].

Experimental data derived from the contact time studies provided the basis used in assuming the pseudo-second order kinetics. The k_2 values at three temperatures were calculated from the slopes of t/q_t against t at 296, 316 and 336 K. The Arrhenius plot of ln k_2 against 1/T for the adsorption of Co(II) on the resin is shown in Fig. 7b. The slope of the plot as extrapolated yielded the Ea value as per the Arrhenius equation. Computed value of E_a (i.e. 5.7 KJ/mol) indicated weak interaction and therefore a physical sorption should be more appropriately considered.

The k_2 values at three temperatures were calculated from the slopes of t/q_t against t at 296, 316 and 336 K. The Arrhenius plot of ln k_2 against 1/T for the adsorption of Ni(II) on the resin is shown in Fig. 7b. The slope of the plot as extrapolated yielded the Ea value as per

the Arrhenius equation. Computed value of E_a (i.e. 15.8 KJ/mol) indicated weak interaction and therefore a physical sorption should be more appropriately considered.

4.4 Reusability

Reusability of the resin is important in economic development because disposing of the exhausted sorbent loaded with the adsorbates may cause environmental impact. Experiments was repeated for 3 similar cycles, using equal dose to establish the resistance of resin to deterioration with repeated applications (i.e. to evaluate reusability). It was found that, resin shows good recovery with approximately stable efficiency. Thus, its feasibility of usage could considered established even though more studies may be required for large scale considerations.

4.5 Treatment of real wastewater samples

A sample of industrial wastewater was used as representative sample for real life evaluations of the resin. The samples were spiked with 0.0 and 20 mgL^{-1} Cd^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+} and then treated with the resins under the optimum conditions. According to the results in Table 5, the activity of the resin was observed to be optimal even with real sample due to its resistance to competing species in the sample. These interesting feature improved the prospects of the resin for this application. Interestingly, the resin can as well remove a highly toxic arsenic from the wastewater.

Table 4. 8 Comparison of Ni(II) concentrations in wastewater sample before and after the treatment with CPZDA

Metal	Original sample ($\mu g\ L^{-1}$)	After treatment ($\mu g\ L^{-1}$)		
		Original sample spiked with Ni(II) and then treated with the adsorbent		
		0	10000 ($\mu g\ L^{-1}$)	20000 ($\mu g\ L^{-1}$)
Ni	2.03	<MDL[a]	1.38	1.84
Co	0.362	<MDL	<MDL	<MDL
Cu	22.1	3.18	2.38	2.82
Zn	9.14	0.028	0.581	1.98
As	8.14	<MDL	<MDL	<MDL
Sb	0.037	<MDL	<MDL	<MDL
Pb	0.453	<MDL	<MDL	<MDL

MDL: the method detection limit

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The study examined three (3) pH-responsive polymers in removing trace metal pollutants from water synthesized by Butler's cyclopolymerization. The polymers are; cross-linked polyzwitterion/dianionic (**CPZDA**), hydrophobic cross-linked Dianionic Polyelectrolyte **(HCDAP)** and Hydrophobic Cross-linked polyzwitterionic acid **(HCPZA*)***. Physical methods of TGA, SEM, EDX, FTIR and ZPA were employed in characterizing the structure, surface morphology and elemental composition of the polymers. **CPZDA** shows an outstanding removal Ni(II) followed by Cr(III), Co(II) and Cd (II). The experimental data fitted Langmuir, Freundlich and Temkin models. Maximum adsorption capacity was found to be 45.5 mgg^{-1} at pH 5.5. The adsorption process fitted pseudo-second order kinetic model well and the mechanism was studied by intraparticle diffusion model. Thermodynamic parameters revealed that the adsorption process was endothermic in nature with activation energy of 15.8 KJ/mol. **HCPZA,** shows efficiency for Co (II) with adsorption capacity was found 76.9 mg/g at optimum pH 6, fitted pseudo-second order model and the adsorption process was endothermic having activation energy of 5.7 KL/moL.

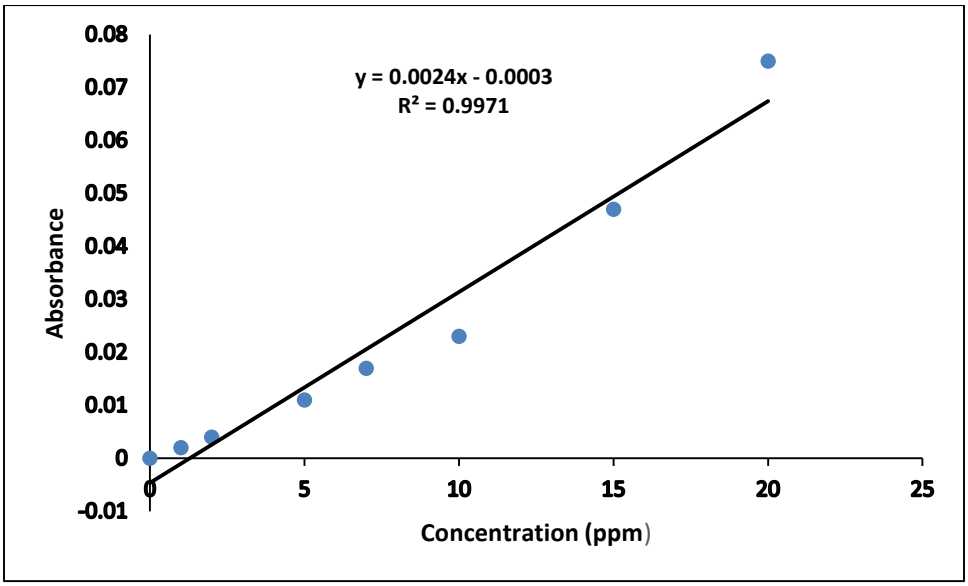
5.2 Recommendations

It is important to highlight some areas that can be further build upon for the in order to serve as a contribution to research and development in the area of water treatment. The following are recommended:

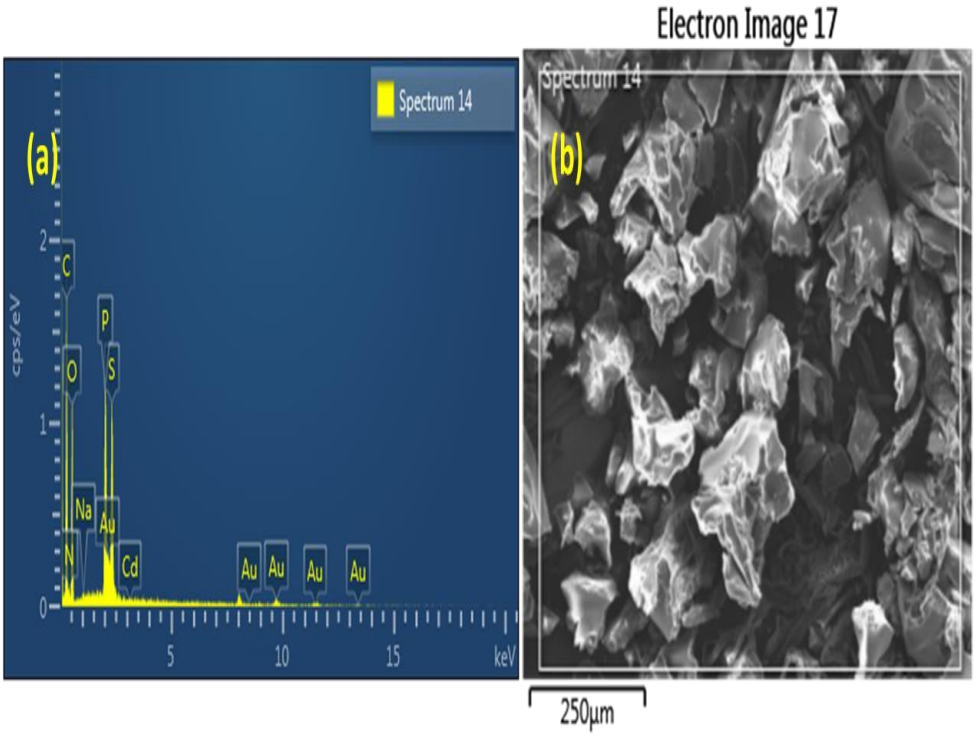
1. A further investigation should be conducted on the efficiency of the polymers using a column system.
2. An XPS studies on the state of the metal species in solution will also help to explain the process further.
3. Different hydrophobes of ionic liquids should be investigated to further strengthen the study for the viability of its application in commercial aspect.
4. A prototype sheet or column should be tested in the university water facility or any other for real water treatment.

APPENDICES

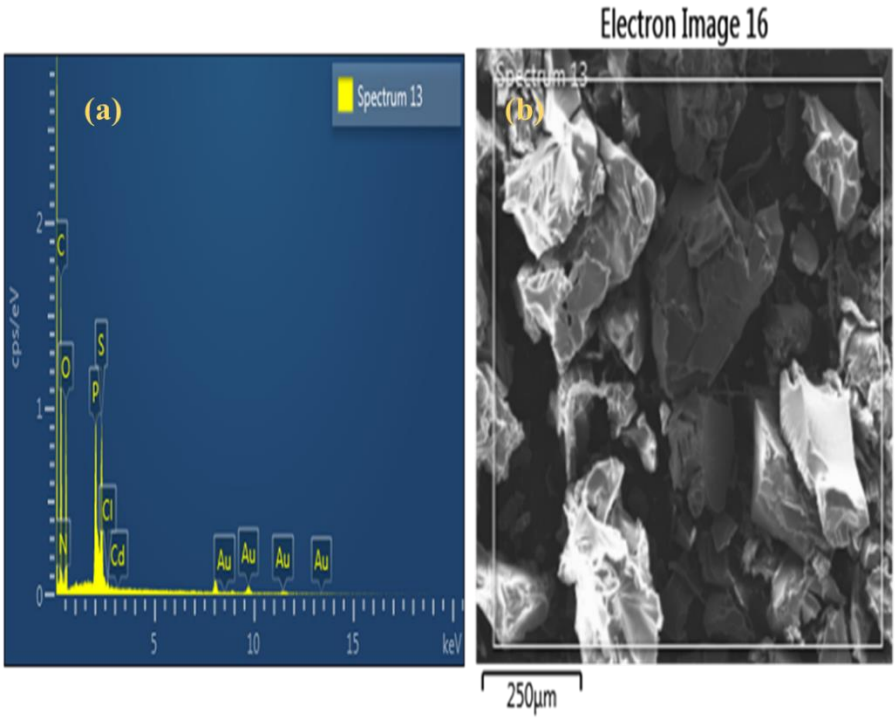
APPENDIX A: CALIBRATION CURVE of Cobalt (II) ion



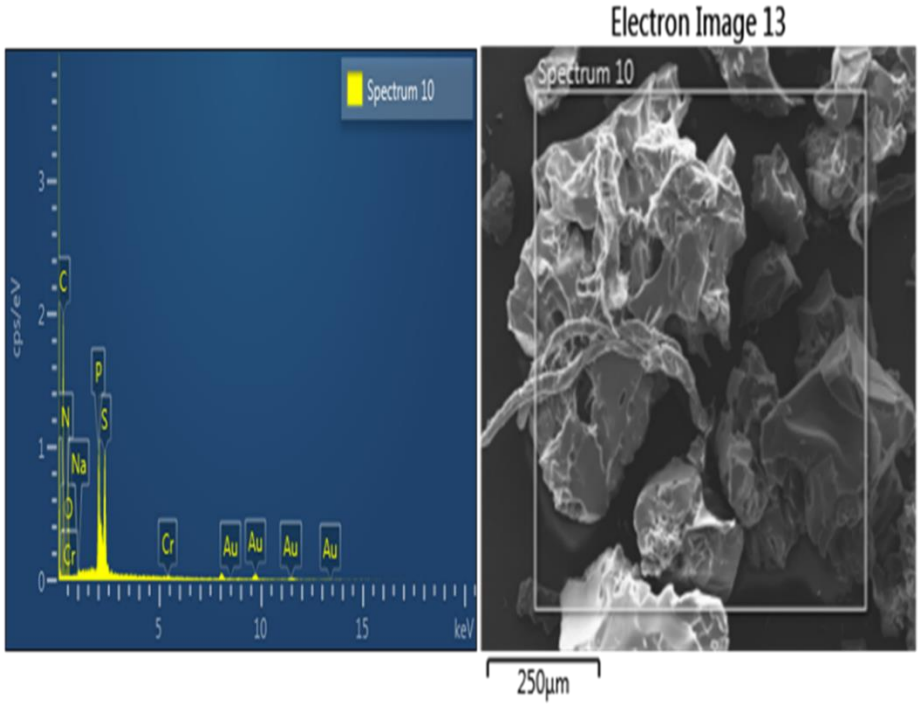
APPENDIX B: SEM-EDX MICROGRAPHS



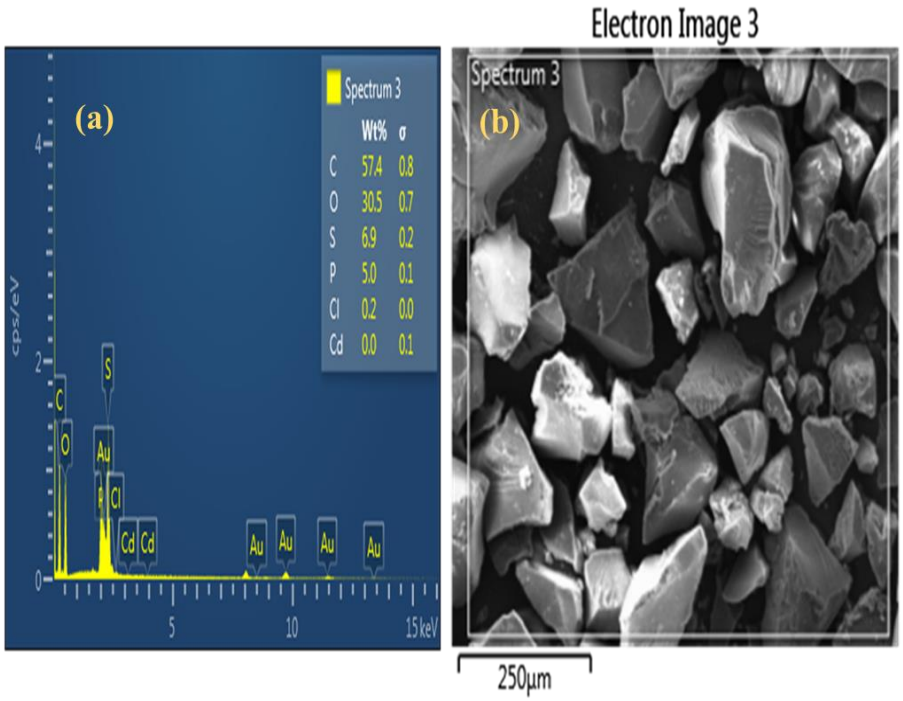
(a) EDX spectrum and the corresponding (b) SEM image of the CPZDA of Cobalt-loaded resin



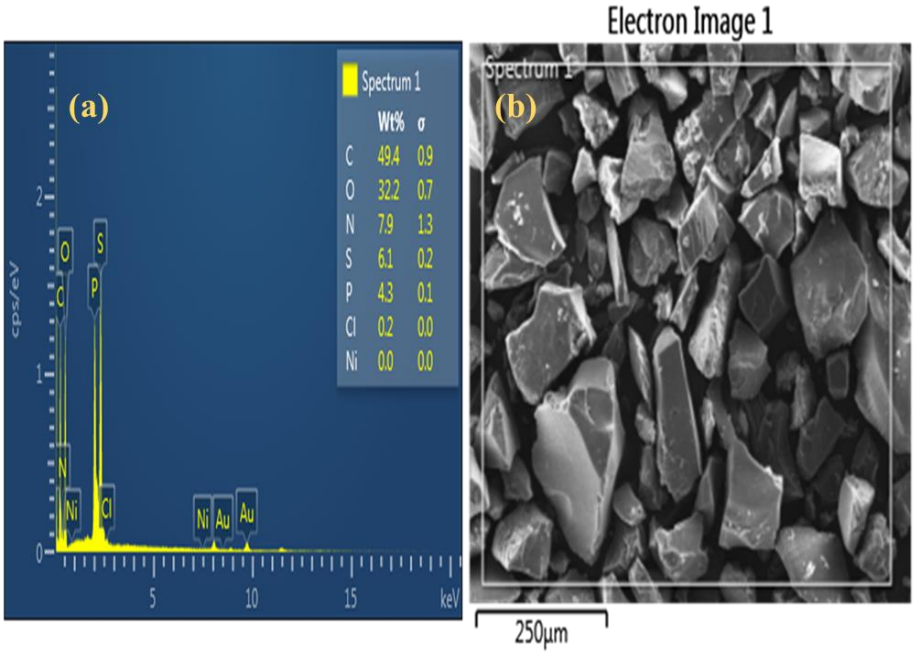
(a) EDX spectrum and the corresponding (b) SEM image of the CPZDA of Cadmium-loaded resin.



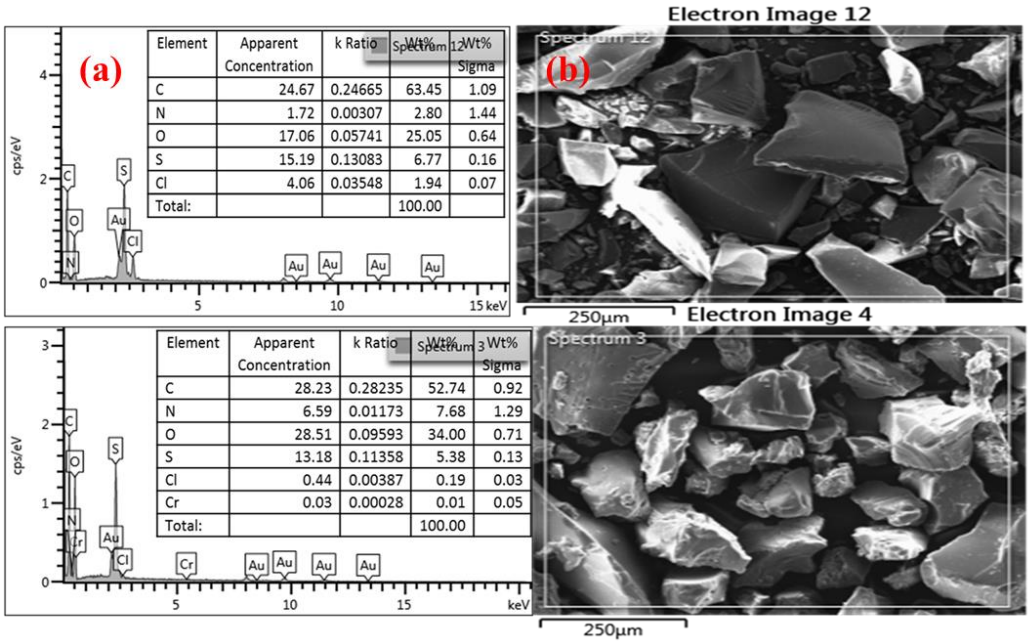
(a) EDX spectrum and the corresponding (b) SEM image of the CPZDA of Chromium-loaded resin.



(a) EDX spectrum and the corresponding (b) SEM image of the HCDAP of Cadmium-loaded resin.



(a) EDX spectrum and the corresponding (b) SEM image of the HCDAP of Nickel-loaded resin.



(a) EDX spectrum and the corresponding SEM image of the HCPZA with a table of quantitative microanalysis; (b) EDX and SEM image of Chromium-loaded resin with a table of quantitative microanalysis.

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